

EXPERIMENTAL STUDY OF HYDRATE FORMATION AND DISSOCIATION PROCESSES OF NATURAL GAS OF GAS-CONDENSATE FIELDS OF EASTERN SIBERIA (REPUBLIC OF YAKUTIA)

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INTRODUCTION

Development of the new gas-condensate and the oil-gas-condensate fields of Eastern Siberia of Russia is planned in the immediate future. A number of deposits of republic of Saha (Yakutia) is characterized by abnormally low reservoir temperature, which is favorable to the gas hydrate formation at the bottom hole formation zone of reservoir. As example is Chayandinskoe oil-gas-condensate field, Tas-Yuryakhskoe oil-gas-condensate field, Verkhnevilyuchanskoe oil-gas-condensate field, Sobolokh-Nedzhelinskoe gas-condensate field etc. (see fig.1). In the course of the field exploitation the hydrate formation both at the bottom hole formation zone of reservoir and in the well shafts is possible. Creation of technology which prevents the hydrate formation at the thermobaric conditions of gas hydrates occurrence is urgent task.

Risk assessment, prediction of nature and dynamics of hydrate formation is based on the knowledge of mechanism of hydrate formation process. This knowledge can be getting through the performing of the specialized comprehensive studies including the experimental simulation of the basic factors which predetermine the process of hydrate formation in the water-saturated porous media.

Up to date experimental method of precision adiabatic calorimetry is used for studying of thermodynamic and kinetic properties of the natural gas hydrate formation and decomposition. This method was realized for an experimental complex, which consists of two adiabatic calorimeters.

The natural gases of a number of oil-gas-condensate fields of republic of Saha (e. g., Botuobinskoe deposits) were investigated. Phase behavior of the hydrocarbon mixtures at the thermobaric conditions of hydrate formation has the complex nature. The thermobaric domain of gas hydrate occurrence is not uniform, but it is divided into the row of the ranges with different crystal structure of hydrates. Phase transitions from one structure of hydrate to another are accompanied by the structural phase transitions.

Based on performed investigations the phase diagrams of gas hydrates of different structures are built. The thermobaric domains of the state of hydrate-free ranges are also defined. The enthalpy diagrams of hydrate formation and hydrate dissociation and phase diagrams of phase transitions between different structures of hydrates are also built. Based of enthalpy diagrams relative quantities of phases formed by hydrates of different structures are determined.

Extensive thermobaric domain of the state of metastability (without the formation of hydrates for a long time) is discovered. Research of sufficient stable region of the metastable state of the intermediate water - hydrocarbons system in the productive reservoir (at the bottom hole formation zone) makes it possible to more reliably evaluate the risks and probability of hydrate formation at the thermobaric conditions of these hydrates occurrence. Experimental results clarifying the mechanisms of hydrate formation and dissociation processes and also phase diagrams are effectively used for selection of the technological regimes of the wells exploitation.

EXPERIMENT

Experimental setup

Method of precision adiabatic calorimetry is used for investigation of hydrate formation and decomposition for natural gases. This method is realized in experimental complex, which consists of two adiabatic calorimeters [1, 2].

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Figure 1. Oil-gas-condensate fields with potential hydrate occurrence in the Eastern Siberia of Russia.

The first calorimeter is used for investigation of fluids in bulk. The second one is used for investigation of fluids in porous media. Measurements of the thermodynamic parameters are made either independently on each calorimeter or simultaneously on both. With the simultaneous work of two calorimeters one and the same fluid are placed both into the cell of the first calorimeter (bulk) and into the cell of the second calorimeter (porous media). Comparison of the measured parameters made it possible to specify the porous medium effect. The schemes of the calorimeter constructions are similar and presented in Figure 2. Differences between the calorimeters consist of the calorimetric cells (1) construction.

The cell for the measurement in bulk having a total volume of about $14.895 \pm 0.02 \text{ cm}^3$ contains the magnetic mixer, which is set in action by solenoid (10) with the period of 10 s. Platinum thermometer (12a) is placed into the copper case inside the cell. The cell for the measurement in the porous medium having a total volume of about $10.667 \pm 0.02 \text{ cm}^3$ is collapsible. Thermometer is placed on its side (12b). The accuracy of the temperature measurement does not exceed 0,0005 K according to the sensor's calibration table.

In other respects the construction of calorimeter cells are similar. Stainless steel cylindrical cells are placed into the copper cans with thin walls. On the surface of each can the electrical heater with the resistance of 100Ω is located.

The basis for the method of precision adiabatic calorimetry is the control and the accurate measurement of the total heat flow released or consumed by the studied sample. This is achieved by providing a good thermal isolation between the experimental cell (1) and the environment due to enclose this cell into the high vacuum. An experimental cell is surrounded by two copper heat screens (2, 3). The communication wires leading to the calorimeter cell are placed and glued on the top screens and on two copper cylindrical blocks (4, 5). The cold conductor (6) thermally connects the thin capillary tube and the block (4). The temperature of the screens, blocks and cold conductor is automatically adjusted to the cell temperature and controlled by a servo system. The temperature-difference sensors are thermocouples (8). The temperature of the inside screens (2) and of the block (4) is equal to that of the calorimeter cell. The temperature of the screen (3) an

temperature of the cell by about 1-2 °C. The temperature of the upper part of the capillary is higher than the temperature of cell by one degree in order to exclude the condensation of mixture in capillary. This construction is held by thin stainless steel capillaries and placed inside of the vacuum jacket (11). The entire setup is placed into a dewar (7) with the liquid nitrogen.

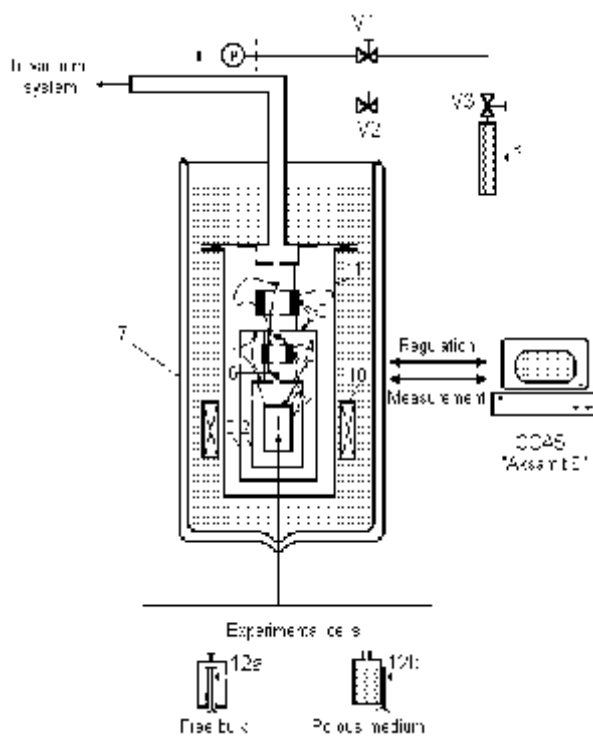


Figure 2. Schematic illustration of the adiabatic calorimeter

Before the experiment, the experimental cell is pumped to a vacuum and then is filled with the studied fluid through the system of thin capillary tubes and valves (V1, V2, V3) from the high-pressure cylindrical sampler (9). The fluid pressure in the cell is measured by the gauge of pressure (P) located in the thermostat (T) with an accuracy of 0,0007 MPa. The temperature and pressure in the cell, the amount of heat applied to the cell are measured and these experimental data are continuously recorded by the computer-controlled acquisition system (CCAS) during the experimental investigation.

Sample preparation

Investigation of gas hydrate formation and decomposition for multicomponent gas mixture was carried out in porous medium. As the porous medium was used quartz sand with the average size of grains 31.5μ and a specific surface $0.104 \cdot 106 \text{ m}^2 / \text{m}^3$. The porous volume was 5.209 cm^3 .

Creation of the water-saturated porous medium was carried out by a procedure submitted in [2]. The non homogeneous water distribution in the porous space was achieved after the water added to the cell from a syringe (cell detached from the calorimeter). For uniform distribution of water over the pore space the cell was heated up to temperature 660 - 670 K (above the critical point of water equal to 647.28 K) and then slowly cooled to the room temperature.

Content of water in the porous medium and in the bulk was measured by two procedures (both methods yield comparable results):

1. By weighing of the cell before and after filling with water.
2. By calorimetric measurements of melting heat of ice formed in a cell.

Water saturation calculated as the share of porous space volume occupied with water varied from 0.224 to 0.253 in the research process.

After placement of the water-filled cell in the plant, the system was cooled

than the ice crystallization temperature. After that, remaining air was pumped out of the cell. At the final stage, the water-filled cell was filled with a hydrate forming gas mixture. Hydrate formation took place directly in the calorimetric cell.

Gas mixture is prepared in the special high-pressure cylindrical sampler using a row of hydrocarbon and non hydrocarbon components. Composition of the six-component gas mixture that closed on hydrate forming components to the composition of natural gas of Chayandinskoye oil-gas-condensate field (Botuobinsky horizon) is represented in Table 1.

Components of the six-component gas mixture, (mol. %)					
CH ₄	C ₂ H ₆	C ₃ H ₈	iC ₄ H ₁₀	CO ₂	N ₂
85.57	4.57	1.55	0.21	0.69	7.41

Table 1. Composition of the six-component gas mixture, (mol. %)

Description of research

Research in kinetics of gas hydrates formation and dissociation from the bulk water is complicated by long duration of the gas diffusion process. A decrease in non-equilibrium of the system caused by long duration of the gas diffusion can be provided by increasing the water - gas interface. It achieved by using porous media.

The required temperature and pressure conditions of the metastable gas-hydrate phase in the calorimetric cell can be achieved by the thermal method [3]. Using this method the two-phase (gas and water) system is cooled isochorically down to the hydrate existence region. During the measurements the following regimes are used:

- the cooling regime (formation and accumulation of hydrate and crystallization of ice),
- the heating regime (melting ice and hydrate),
- the relaxation regime (it was investigated the kinetics of the system relaxation to the state of equilibrium).

STATE OF DOUBLE METASTABILITY OF WATER – HYDROCARBON SYSTEMS

Based on our experimental data [4] one can conclude that state of metastability of the water – gas system precedes the phase transitions to the stable solid phase: hydrate or ice. Knowing the thermal history of water it is possible to predict positively the direction and the nature of these phase transitions.

The series of water states should be determined as the following:

- “fresh water” - water, for the first time injected in the porous medium,
- “thawed water” - ice passed into a liquid water (melted ice),
- “water of molten hydrate” - hydrate passed into a liquid water.

Our last studies are showed, that effect of the water thermal history on the process of hydrate formation has general nature and is observed both for individual hydrocarbon and non hydrocarbon components and for their mixtures including natural gas.

Experimental data of the water thermal history effect on process of hydrate formation for six-component gas mixture are represented further. Composition of gas mixture is shown in Table 1.

Hydrate formation processes in systems with the fresh water and with the molten hydrate water are of a special practical interest. Effect of the thermal history of water on process of hydrate formation is manifested in two forms.

1. Formation of the equilibrium structures *sI*, *sII* and also metastable struc

2. Selection of the phase transition trend from the state of metastability of the water - gas mixture system to the state of equilibrium of solid phase (hydrate or ice).

In the previous two sections effect of the thermal history of water on formation of equilibrium and metastable structures of hydrates was described.

Effect of the thermal history of water upon the trends and the nature of phase transitions from the state of metastability of the water - six-component gas mixture system to the state of equilibrium of solid phase (hydrate or ice) are represented in Fig. 3 and 4. Data for the water – propane system are shown for comparison.

Behavior of the fresh water - gas mixture system during crystallization of ice and during subsequent formation of hydrate is similar to the fresh water – propane system. In subzero temperature zone first occurs crystallization of ice with the heat liberation (BC and B'C', see Fig. 3). Further, during the isochoric cooling, after the induction period (CD and C'D') transformation of ice into hydrate (DE and D'E') occurs.

Behavior of the molten hydrate water - gas mixture system during formation of hydrate and during subsequent crystallization of ice is similar to the molten hydrate water – propane system. In subzero temperature zone first occurs formation of hydrate (BC and B'C', see Fig. 4). Ice is not formed.

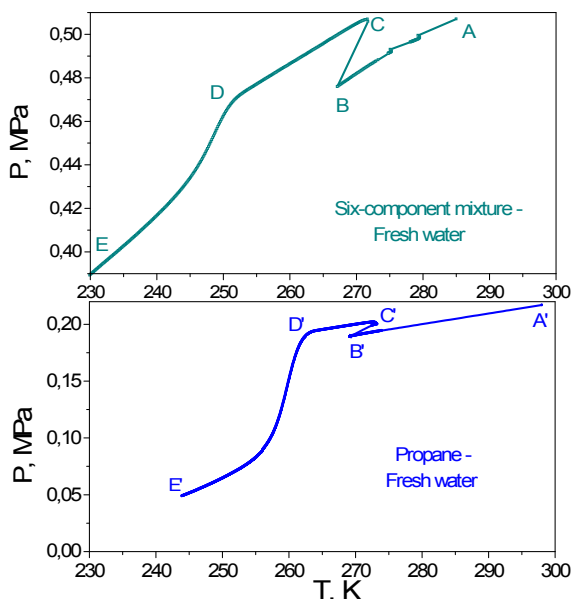


Figure 3. Effect of the thermal history of water on evolution of the state of double metastability of the systems: fresh water - gas mixture and fresh water - propane.

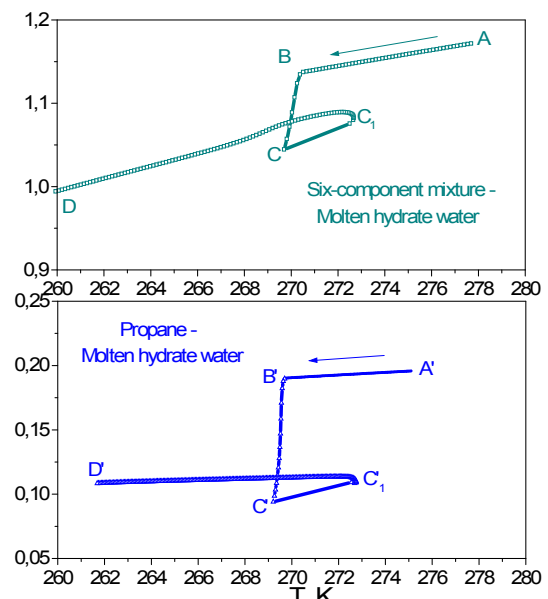


Figure 4. Effect of the thermal history of water on evolution of the state of double metastability of the systems: molten hydrate water - gas mixture and molten hydrate water - propane.

During the hydrate formation a pressure is decreased. At points C and C' crystallization of water with the heat liberation begins. The systems get hot during the crystallization (CC₁ and C'C₁) and become metastable. The partial dissociation of hydrate is carrying out. After crystallization the state of equilibrium of the ice – water system is reached, that is contiguous to the metastable phase of hydrate (C₁ and C'₁). In the course of the further isochoric cooling (C₁D and C'₁D') the systems reaches equilibrium curve ice – hydrate – propane or ice - hydrate - gas mixture.

EQUILIBRIUM CURVES OF WATER – GAS MIXTURE SYSTEM

Measurements of equilibrium curves of the water – gas mixture system are based on the original procedure registered in the Russian scientific and technical centre of information on standardization, metrology and assessment of conformity [1]. Phase transition is accompanied by the anomalous behavior of the thermodynamic parameters (thermodynamic derivatives, heat capacity). This fact is used to localize the temperature and the pressure characteristics of phase 1

Alteration of the thermodynamic derivative $(dP/dT)_V$ during the hydrate decomposition is shown in Fig. 5. Hydrates of structures *sI* and *sII* were prepared from fresh water (E_1E_2) and from molten hydrate water ($F_1F'_2F''_2$). Extrema E_1 and F_1 correspond to decomposition of hydrate structure *sI*. Extrema E_2 and F_2 correspond to decomposition of hydrate structure *sII*. Equilibrium curves for the water – hydrate – gas transition were measured during the process of hydrate dissociation. Results of the equilibrium curve measurements for the water (ice) – hydrate (*sI*, *sII*) – gas mixture system are represented in Fig. 6. Line AB corresponds to equilibrium of the water (ice) – hydrate *sI* - gas mixture system. Line CD corresponds to equilibrium of the water (ice) – hydrate *sII* - gas mixture system.

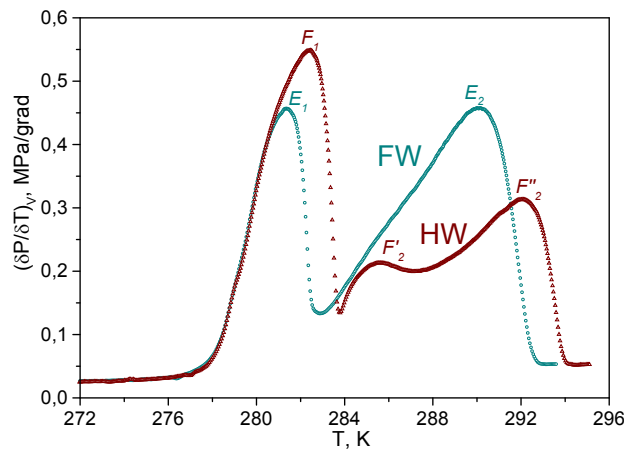


Figure 5. Measurements of thermodynamic derivative $(dP/dT)_V$ during the system heating (hydrate decomposition).

Character of hydrate formation is predetermined by the thermal history of water (see [4]). The state of metastability of the fresh water – gas mixture system is transformed into hydrate structure *sI* and *sII*. Lines AB and CD in Fig. 6 and also points E_1 and E_2 in Fig. 5 correspond to decomposition of these structures. The state of metastability of the molten hydrate water – gas mixture system is also transformed into hydrate structure *sI*. But line, which corresponds to the hydrate structure *sII* decomposition (CD), splits on two lines (EF and GI), accordingly points F'_2 and F''_2 in Fig. 5.

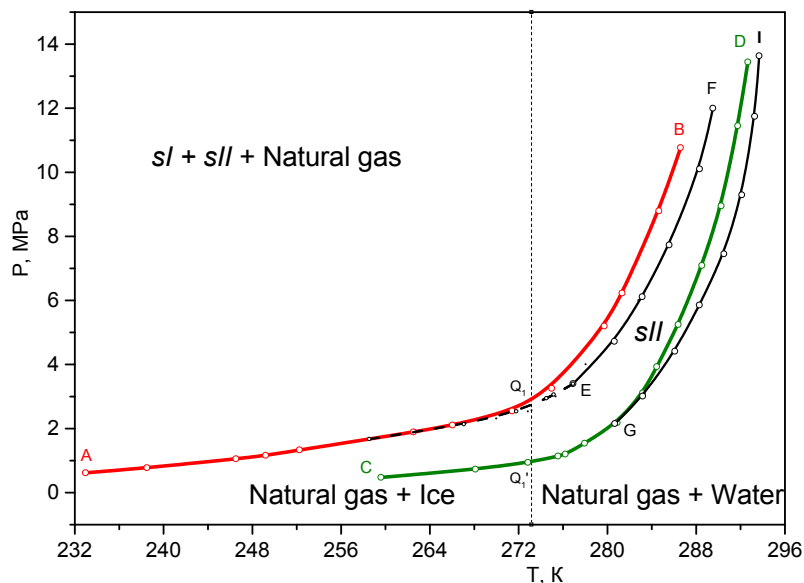


Figure 6. P – T diagram of hydrate decomposition for the six-component gas mixture

Data of the temperature decomposition and the pressure decomposition of structure *sII* is of a special practical interest. These values take into account as thermobaric conditions of hydrate decomposition (line CGI in Fig. 6). Experimental data are represented in Table 2.

T, K	270.01	272.84	275.56	276.21
P, MPa	0.824	0.942	1.139	1.201

T, K	277.95	280.7	283.19	286.08
P, MPa	1.538	2.152	3.011	4.410

T, K	288.30	290.51	292.12	293.3
P, MPa	5.854	7.452	9.293	11.74

Table 2. Thermodynamic conditions of the solid phase decomposition.

LATENT HEAT FOR WATER – HYDRATE - GAS MIXTURE TRANSITION

Process of hydrate decomposition or formation is a first-order phase transition and is accompanied by the consumption or releasing of heat, the amount of which is the key characteristic of this transition. The latent heat of hydrate dissociation can be found from the heat capacity measurement. Measurement of the heat capacity is independent of measurement of the thermodynamic derivative $(dP/dT)_V$ and complements its. Behavior of the heat capacity (fig. 7) is similar to behavior of the thermodynamic derivative $(dP/dT)_V$ (Fig. 5), as they describe the same process in the same system.

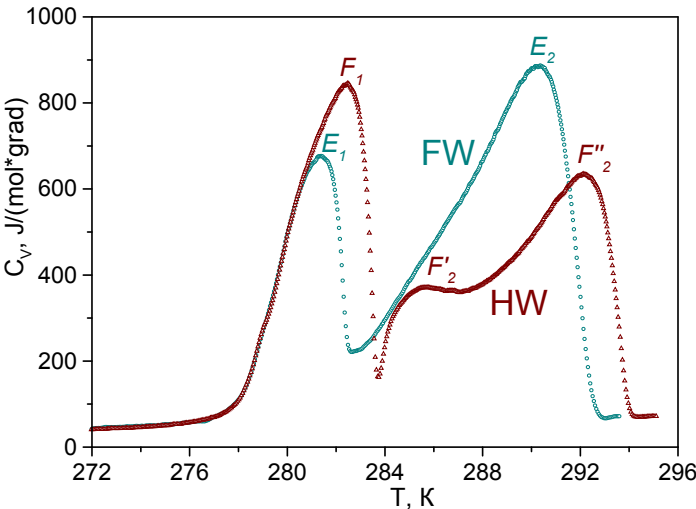


Figure 7. Heat capacity measurements during the hydrate decomposition (heating).

Enthalpy change during decomposition of hydrate structure *sI* and *sII* prepared from the fresh water (ABCD) and prepared from the molten hydrate water (ABC'D') is shown in Figure 8. Quantity of water in the porous medium determined by calorimetric measurements is 1.16790 g. Volume of the free porous space is 4.29 cm³. Density of gas mixture is 91.876 kg/m³. This is typical lines for the hydrate decomposition with the high density of gas mixture. All water is transformed into hydrate. Total melting heat of hydrate structures *sI* and *sII* (620.95 J) prepared from the molten hydrate water is greater by 2 – 2.5% than total melting heat of hydrate structures *sI* and *sII* (606.19 J) prepared from the fresh water. Quantity of hydrate structures *sI* prepared from the molten hydrate water is 1.63 as much of quantity of hydrate structures *sI* prepared from the fresh water. Quantity of hydrate structures *sII* prepared from the fresh water is 1.25 as much of quantity of hydrate structures *sI* hydrate water.

Typical enthalpy for the ice melting (AB) and for the hydrate decomposition (BCD and BC'D') with the low densities of gas mixture is shown in Fig. 9. Density of gas mixture is 58.124 kg/m^3 .

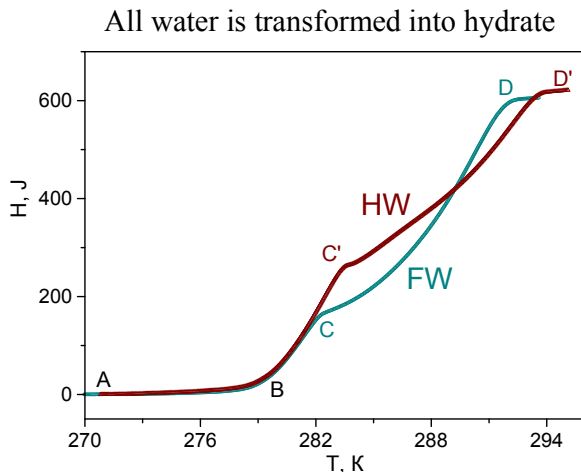


Figure 8. Enthalpy for hydrate decomposition with the high density of gas mixture

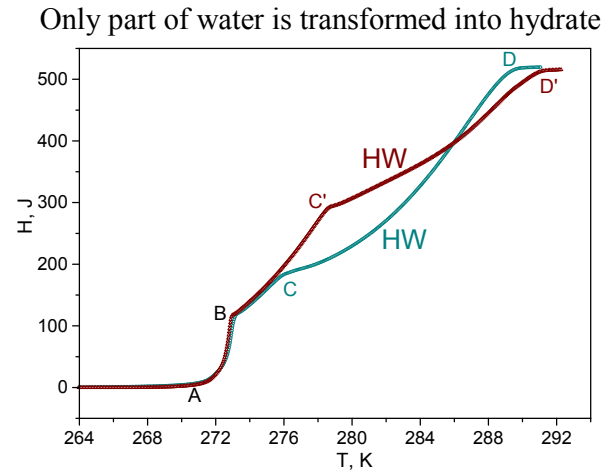


Figure 9. Enthalpy for ice melting (AB) and for hydrate decomposition (BCD, BC'D') with the low density of gas mixture

Enthalpy versus temperature for a number of isochors (value densities represented as $[\text{kg/m}^3]$) is represented in Fig. 10. Boundaries of coexistence of the structures *sI* and *sII* prepared from fresh water (CD) and from molten hydrate water (AB) are shown. As can be seen from Fig. 10, if the pressure (density) of the hydrate-forming gas mixture is increased, a relative quantity of hydrate of structure *sI* decreases but a relative quantity of hydrate of structure *sII* grows.

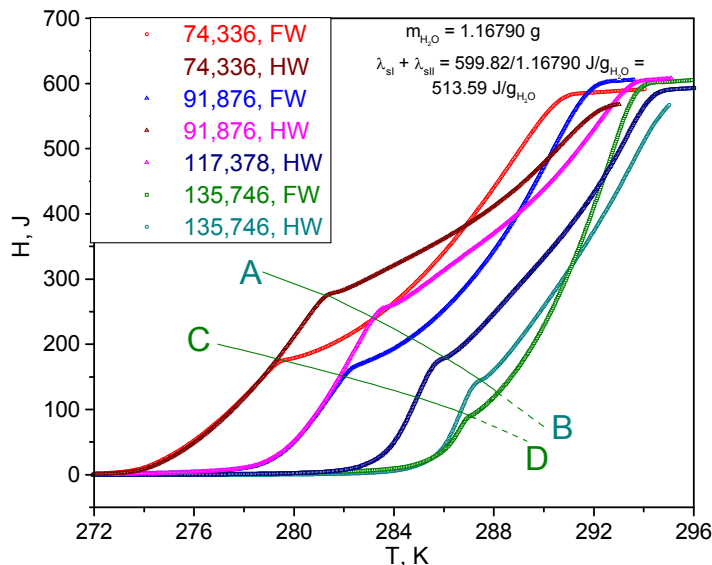


Figure 10. Enthalpy change during decomposition of the gas mixture hydrate.

HYDRATE FORMATION AT BOTTOM-HOLE ZONE

Russian oil-gas-condensate fields of republic of Saha (Yakutia) at East Siberia are characterized by abnormally low reservoir temperature (below 285 K) and initial pressure at the range of $13\text{--}15 \text{ MPa}$. In spite of these thermodynamic conditions there is no gas hydrates in porous media of the reservoir due to high salinity of formation (residual) water (up to $300\text{--}400 \text{ g/l}$). As for hydrates at bottom-hole zone the process of hydrate formation is really possible because of water vapor condensation from flowing gas and desalinization process of formation water. So in the course of the field exploitation the hydrate formation both at the bottom-hole zone and in the product

technology which prevents the hydrate formation at bottom-hole zone at the thermobaric conditions of gas hydrates occurrence is important problem.

At figure 11 a calculated hydrate line for gas composition close to botuobin horizon of Chayanda gas condensate field is presented (correlation by different thermodynamic methods with additional empirical correction using our experimental data, see Table 2) . Due to relatively high quantity of ethane, propane, butane (amounting to 5-6 %, see Table 3) lead to the fact that deposit should be consists of gas hydrates, at that temperature’s approach to a hydrate zone of a phase diagram is sufficiently great (to 10-12 degrees Celsius). A high salinity of formation water on the level of a few hundreds g/l is a typical for gas-condensed fields of Western Siberia. So this is the reason of prevention of hydrate formations in-situ (self-inhibited deposits).

Components	Mol. %
Methane	85,82
Ethane	4,56
Propane	1,56
iso-Butane	0,21
n-Butane	0,49
Sum C ₅₊	0,27
Carbone dioxide	0,19
Nitrogen	6,43
Hydrogen	0,04
Helium	0,43

Table 3 Botuobin formation average gas composition (East Siberia)

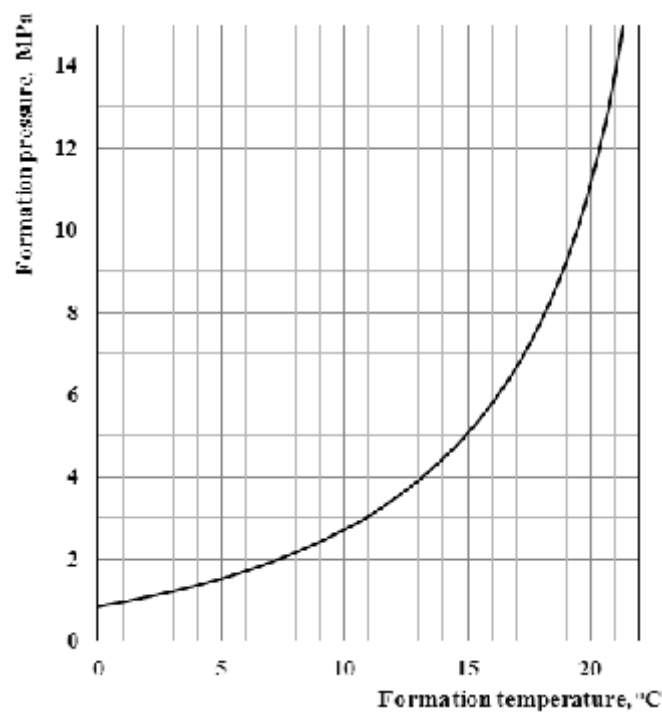


Figure 11. Hydrate conditions botuobin horizon of Chayanda gas excluding water salinity (for pure water)

By using thermodynamic analyses it was obtained that a very good correlation with water activity in different salt solutions is take place. At figure 12 the gas hydrate formation conditions with different salt concentration in water solutions (in g/l). So if salts in form

350 g/l there is a “reserve” in hydrate formation’s temperature about 16 degrees Celsius (it means that there is no gas hydrates in situ at botuobin deposits of East Siberia gas-condensate fields).

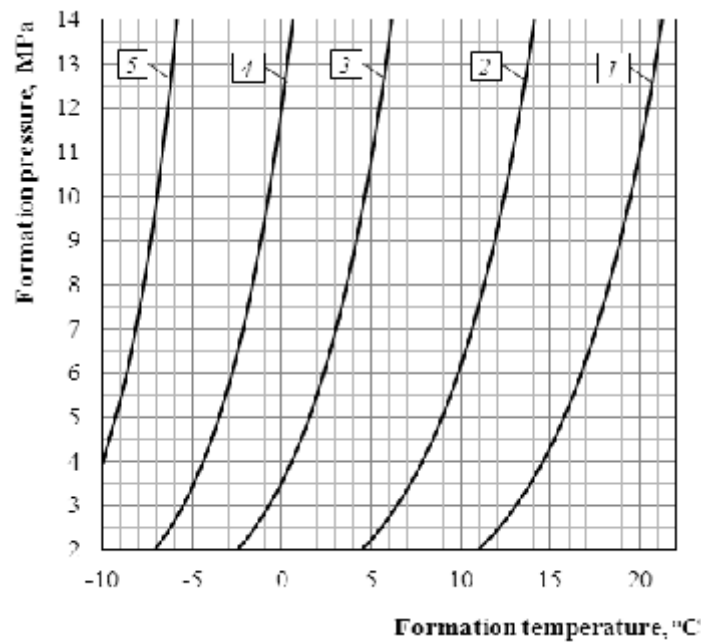


Figure 12. Gas hydrate conditions of a botuobin deposits of Chayandin gas fields. Salt concentration of formation water: 1 – 0 g/l, 2 – 150 g/l, 3 – 250 g/l, 4 – 300 g/l, 5 – 350 g/l.

Due to water vapor condensation near the wellbore, the salt concentration in pore water will be reducing. But this process, depending on the degree of dilution, temperature and pressure conditions, don't exclude the hydrates accumulation at sufficiently high depression. According our calculations, if the prassure depression is not sufficient to hydrate accumulation in the bottom-hole formation zone, a stationary profile salt concentration in pore water is establishing (Figure 13) from the initial value far of the wellbore up to some smaller value near the bottom hole. After stationary state is established the water vapor condensation from the filtrated gas is finishing. Some experimental data indicates that the salts in reservoir can be not only in dissolved form, but also in the crystalline form. In other words, there is an equilibrium "crystalline salt - solution (brine)" in porous media. In this case, before hydrate formation should take place dissolving crystalline salts. Initially, until there is salt in crystalline form, the water condensation will be supported equilibrium (constant) concentration along the bottom-hole formation zone. Then follow the above-mentioned mechanism of hydrate formation. When pressure depressions exceeding non-hydrate value, also stationary distribution of salt concentration in pore water is established. However, in the possible hydrates formation zone water condensation from the filtrated gas proceeds directly to the solid hydrate phase (Figure 13).

For long-life wells exploitation at different reservoir temperatures we calculate of hydrateless depressions at bottom-hole zone, figure 14. For example, hydrateless depression doesn't exceed 0,4 MPa in case of reservoir temperature is 15 degrees Celsius and residual water's salinity in formation is 200 g/l. So in this case operational wells work with hydrate accumulation at bottom hole zone if hydrateless depression exceeds 0.4 MPa. If salinity of formation water more than 300 g/l, hydrateless depression is more than 1.1 MPa. With salinity 350 g/l the hydrateless depression is 1.6 MPa.

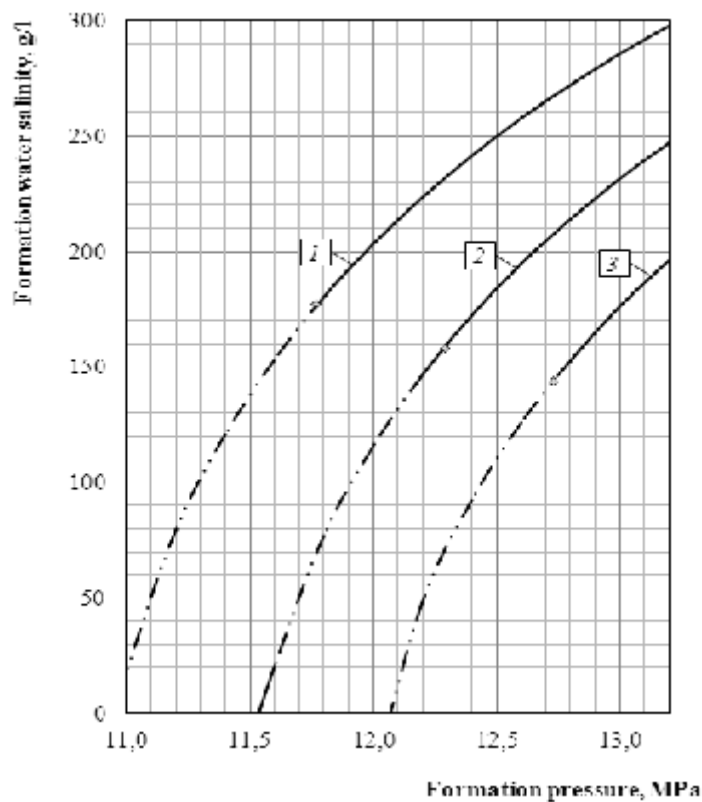


Figure 13. Salt's steady state concentration in pore residual water via gas pressure around exploitation wells at isenthalpic gas flow
 A residual water's salinity in formation: 1 – 300 g/l, 2 – 250 g/l, 3 – 200 g/l.

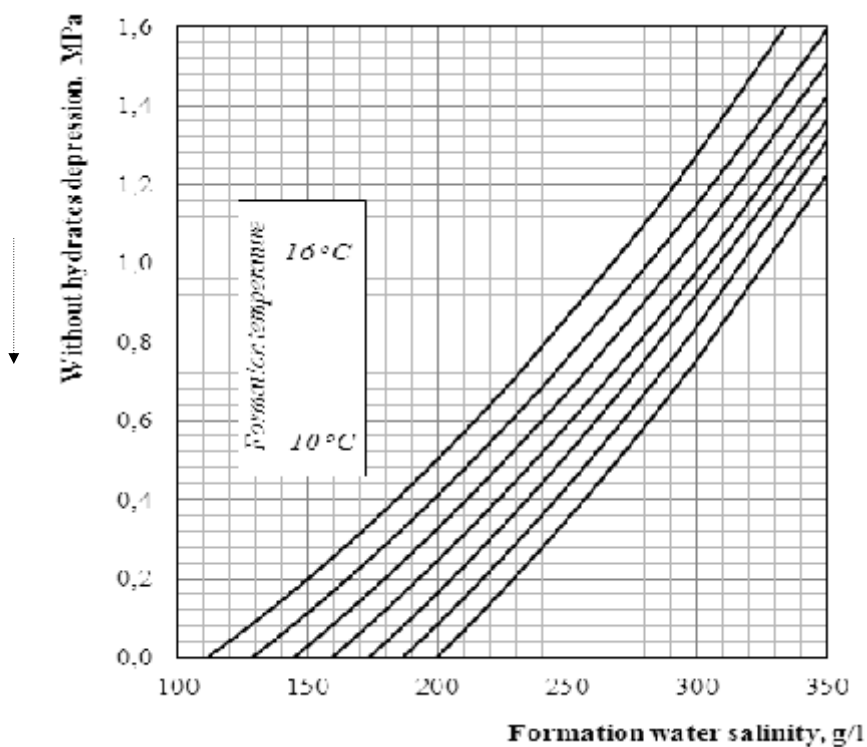


Figure 14 Hydrateless depression for exploitation wells at formation's temperatures from 10 degrees Celsius to 16 degrees Celsius

CONCLUSION

It has been shown that the applicability of a powerful experimental technique such as precision adiabatic calorimetry gives us the possibility of study both thermodynamics and kinetics of the natural gas hydrate formation and dissociation. Also it gives the tool for investigation of the water thermal history effect on behavior of the water – hydrocarbons systems at the thermobaric conditions of hydrate formation.

Phase behavior of the hydrocarbon mixtures at the thermobaric conditions of hydrate formation has the complex nature. The thermobaric domain of gas hydrate occurrence is not uniform, but it is divided into the row of the ranges with different crystal structure of hydrates. Phase transitions from one structure of hydrate to another are accompanied by the structural phase transitions.

There is an extensive thermobaric domain of the state of metastability (without the formation of hydrates for a long time). Research of sufficient stable region of the metastable state of the intermediate water - hydrocarbons system in the productive reservoir (at the bottom-hole zone) makes it possible to more reliably evaluate the risks and probability of hydrate formation at the thermobaric conditions of these hydrates occurrence.

Obtained experimental results clarifying the mechanisms of hydrate formation and dissociation processes as well as phase diagrams may be effectively used for selection of the technological regimes of the gas wells exploitation. Also experimental data is used for determination of allowed depression which provide non-hydrate regime of bottom-hole zone. If depression is higher than the thermodynamic allowed depression the process of hydrate accumulation at bottom-hole zone is possible. But simulations are shown that the process of desalinization is extremely slower. So the production well may work for a long time without bottom-hole hydrates at acceptable outputs of the wells.

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