

Досліджено вплив тиску та температури середовища газової бульбашки на процес гідратування. Запропоновано математичну модель, яка враховує інерційну та термодинамічну складові осциляції газових бульбашок у рідині. Встановлено, що швидкість гідратування набуває максимальних значень під час розігріву газового середовища всередині бульбашки. Отримана залежність швидкості гідратування від температури газу. Результати досліджень можуть застосовуватися для оптимізації технологічних процесів, пов'язаних з промисловим одержанням газових гідратів

Ключові слова: газові гідрати, газова бульбашка, фазові перетворення, тиск газу, температура газу

Исследовано влияние давления и температуры среды газового пузырька на процесс гидратообразования. Предложена математическая модель, учитывающая инерционную и термодинамическую составляющие осцилляции пузырьков газа в жидкости. Установлено, что скорость гидратообразования достигает максимальных значений во время разогрева газовой среды внутри пузырька. Получена зависимость скорости гидратообразования от температуры газа. Результаты исследований могут использоваться для оптимизации различных технологических процессов, связанных с промышленным получением газовых гидратов

Ключевые слова: газовые гидраты, газовый пузырек, фазовые переходы, давление газа, температура газа

STUDY OF THE EFFECT OF THERMOBARIC CONDITIONS ON THE PROCESS OF FORMATION OF PROPANE HYDRATE

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1. Introduction

Thermodynamic processes, which occur on a surface of steam-and-gas bubbles, play a key role in many advanced industrial technologies. These are obtaining of hydrate of natural gas [1, 2] for transportation and storage, desalination of seawater with a help of isobutane hydrate [3, 4], production of heat-insulating materials [5] by method of swelling, mixing of colloidal solutions, and many others.

It is convenient to transport and to store natural gas when it takes the form of gas hydrate. Under natural conditions and technological processes, formation of gas hydrates often occurs on a surface of gas bubbles in water under certain thermobaric conditions [6, 7]. A change in a composition of a gas, in a size of a bubble (oscillation), in temperature of a gas medium and a surface of a liquid accompanies the process of hydration. There is a very rapid change in thermodynamic parameters of the system “gas bubble – liquid – gas hydrate” during the oscillation. The study of the dynamics of phase transition processes on a surface of an oscillating gas bubble is relevant due to the need to optimize the technology of obtaining of gas hydrates.

Direct observation of processes inside a bubble during formation of gas hydrates is a complex engineering and tech-

nological problem. Such bubbles are small in size (10^{-3} – 10^{-4} m), they have high pressure (up to 20 MPa) and high oscillation rate (approximately 10^{-5} s). Therefore, tools of mathematical modeling are widely used for the study of heat and mass transfer processes, which occur during hydration. However, such a mathematical model should take into account all thermodynamic peculiarities of this complex process.

2. Literature review and problem statement

Scientists widely use the Rayleigh-Plesset equation to analyze dynamics of oscillations of steam bubbles [8, 9]. They often use Clapeyron-Clausius equations to determine a pressure inside a steam bubble [10, 11], or consider a process as adiabatic process [12]. According to other scientists, processes inside an oscillating bubble are not limited to the phase transition or the lack of heat exchange on a surface of a bubble only. A mathematical statement of the problem is more complete in papers [13, 14]. In addition to the Rayleigh-Plesset equation, it contains the van der Waals equation for determination of a pressure inside a steam-and-gas bubble and makes possible to calculate temperature of gases inside a bubble on the basis of the first law of thermo-

dynamics. Also, transfer of heat and mass across the boundary of a bubble supplements a mathematical model. However, the mathematical model is designed for bubbles formed as a result of cavitation, and there is a highly discharged gas inside them. A paper [15] does not take into account phase transitions in a liquid, and in a work [6] a heat conductivity equation for a flat side describes a transfer of heat in a liquid, which surrounds a gas bubble. In determination of thermodynamic characteristics of a gas medium of a bubble, a number of authors take a constant temperature of a liquid: when calculating cavitation [10], gas [7] and steam [12] bubbles, swelling of materials [5].

To simulate processes of formation of gas hydrates, it is necessary to take into account a possibility of dissolving of bubble gases in a liquid with the simultaneous phase transition of a liquid into a solid phase (gas hydrate). A rate of heat and mass transition processes near a surface of a bubble determines the process of hydrate formation. Heat and mass transition processes, in turn, depend on a temperature and pressure of a gas mixture inside a bubble. Thermophysical characteristics of a liquid on a border with a bubble can also change significantly due to the hydrate formation. Thus, for the correct formulation of the problem, it is necessary to take into account a complex of interconnected mechanical and thermodynamic processes that proceed at high speed in a limited volume of a gas bubble.

3. The aim and objectives of the study

The objective of present work is to study the influence of initial temperature and pressure of the gas medium of a bubble on the processes of hydrate formation. This will make it possible to optimize the technology of industrial processes of hydrate formation. We set the following tasks to achieve the objective:

- to supplement a mathematical model of a gas bubble by a description of the diffusion processes on a gas-liquid boundary, of the phase transition and the hydrate formation processes in a liquid;
- to carry out calculations of transition thermodynamic processes inside an oscillating gas bubble and hydrate formation at different initial temperatures of the propane-butane mixture;
- to calculate the hydrate formation on a surface of a bubble at different initial pressures of a gas mixture and constant initial temperature of a gas.

4. Mathematical model of bubble hydrate formation

To obtain calculation data on a rate of hydrate formation on a surface of a gas bubble, we use a mathematical model, which contains the following simplifying assumptions:

- a gas bubble is spherical;
- a liquid is viscous and incompressible;
- there is a mixture of gases (propane and n-butane) inside a gas bubble, it's mass may change as a result of mass transition processes on a border of a bubble;
- we consider gases in a middle of a bubble as a real gas (taking into account the van der Waals forces) [13].

We consider equations, which describe the behavior of a steam-and-gas bubble in the transition to a new state of the thermodynamic equilibrium. We will record the inertial

component of a gas bubble in a mathematical model with the help of the Relay-Plasset equation [8, 9]

$$\frac{d\dot{R}}{d\tau} = \frac{P_{B(\tau)} - P_{\infty}}{\rho_r R} - \frac{1.5}{R} \dot{R}^2 - \frac{4\mu_r}{\rho_r \cdot R^2} \dot{R} - \frac{2\sigma_r}{\rho_r \cdot R^2}, \quad (1)$$

where R is the radius of a gas bubble, m; τ is time, s; P_B is the pressure of a gas mixture inside a bubble, Pa; P_{∞} is the pressure in a liquid, Pa; ρ_r is the liquid density, kg/m³; μ_r is the dynamic viscosity of liquid, Pa·s; σ_r is the coefficient of surface tension of a liquid, N/m.

We can neglect a small amount of water steam in the propane-butane mixture. Then the radius of a bubble will change only at the expense of a radial movement of the bubble side. The velocity of the liquid (\dot{R}) at the boundary of a bubble can be determined by the formula

$$\frac{dR}{d\tau} = \dot{R}. \quad (2)$$

The total pressure inside a bubble will be equal to the sum of partial pressures of individual gases according to the Dalton's law:

$$P_B = P_b + P_p, \quad (3)$$

where P_b , P_p are the partial pressures of butane and propane, respectively, Pa.

The gas pressure varies widely in result of changes in a size, temperature and composition of the steam-and-gas mixture of a bubble. We use the van der Waals equation to take into account properties of real gases in the determination of pressure

$$P_b = \frac{R_{\mu} T}{\frac{\mu_b}{\rho_b} - b_b} - \rho_b^2 \frac{a_b}{\mu_b^2}, \quad P_p = \frac{R_{\mu} T}{\frac{\mu_p}{\rho_p} - b_p} - \rho_p^2 \frac{a_p}{\mu_p^2}, \quad (4)$$

where ρ_b , ρ_p are the densities of butane and propane, kg/m³; $R_{\mu} = 8314$ is the universal gas constant, J/(Kmol·K); μ_b is the a molecular weight of butane, kg/kmol; μ_p is the molecular weight of propane, kg/kmol; T is the temperature of mixture of gases in a bubble, K; a is the constant of van der Waals, (H·m⁴)/mol²; b is the constant van der Waals, m³/mol. Equation (4) can be replaced by modifications of the Van der Waals equation (Redlich-Kwong, Wilson or Soave) in some cases in order to improve the accuracy of a calculation.

It is necessary to know a density of gases inside a bubble at any given time to solve the equations (4). In the case of mass transition processes on a surface of a bubble, the density of each component of a gas mixture can be found by integrating of corresponding equations

$$\frac{d\rho_b}{d\tau} = \frac{3}{R} \left(I_b - \rho_b \frac{dR}{d\tau} \right), \quad \frac{d\rho_p}{d\tau} = \frac{3}{R} \left(I_p - \rho_p \frac{dR}{d\tau} \right), \quad (5)$$

where I_b , I_p are the masses of steam of butane and propane, which diffuse through a unit of a bubble surface per unit of time, kg/(m²s).

The first law of thermodynamics is used usually to determine temperature inside a steam bubble. For a mixture of two gases it looks as follows

$$\frac{dT}{d\tau} = \frac{3}{R(c_b \rho_b + c_p \rho_p)} \left[q - P_B \frac{dR}{d\tau} \right], \quad (6)$$

where c_b, c_p is the heat capacity of butane and propane, J/(kg·°C); q is the specific heat flow directed from a side to a gas medium of a bubble, W/m².

A prerequisite for the occurrence of a heat flow is the difference in temperature between a side of a steam bubble and a gas mixture in the middle of a bubble. The total specific heat flow (q) consists of the following parts:

- a heat flow with molecules, which move from a gas mixture to a side of a bubble;
- a heat flow with molecules of gases, which were reflected from a side of a bubble and evaporated from it and move inside a bubble;
- a heat flow, which comes from a gas medium to a side of a bubble with gas molecules that are absorbed on this surface. In general, the equation for determination of the specific heat flow looks as:

$$q = \left[\left(\frac{1}{6} \rho_p \bar{v}_{p(T)} + I_p \right) c_p + \left(\frac{1}{6} \rho_b \bar{v}_{b(T)} + I_b \right) c_b \right] (T_{(R,\tau)} - T), \quad (7)$$

where $\bar{v}_{(T)}$ is the arithmetical mean velocity of gas molecules at T temperature, m/s.

Formulas known from the molecular-kinetic theory of gases determine the arithmetical mean of heat motion of propane and butane molecules, m/s

$$\bar{v}_{p(T)} = \sqrt{8R_\mu T / \mu_p \pi} \quad \text{and} \quad \bar{v}_{b(T)} = \sqrt{8R_\mu T / \mu_b \pi}. \quad (8)$$

There are two known modes for determination of the mass flow at a surface of a bubble: diffusion and hydrate formation.

We can consider a rate of diffusion of propane and butane into water as constant when considering small intervals of time (about 200 μs). Then, based on Fick's first law, we determine the specific mass flow of diffusing gases by the formulas:

$$I_p = -\frac{D_p P_p}{R\Gamma_p} \quad \text{and} \quad I_b = -\frac{D_b P_b}{R\Gamma_b}, \quad (9)$$

where D_p, D_b are diffusion coefficients of propane and butane, respectively, m²/s; H_p, H_b are the Henry constants for propane and butane, respectively (Pa·m³)/kg. The sign “–” in formula (9) shows that a gas medium of a bubble “loses” a part of gas.

Since we have only a propane as a hydrate forming gas in the test mixture, we can determine the specific mass flow of this gas during the hydration process by the formula

$$\Delta I_p = \frac{2D_p}{R} (\rho_{gp}^* - \rho_p), \quad (10)$$

where ρ_{gp}^* is the propane density on a hydrate formation line, kg/m³.

The density of the gas near a surface of the hydrate can be determined by the van der Waals equation

$$\rho_{gp}^* = \frac{\mu_p}{R_\mu T} + b_p \left[P_p^* + (\rho_{gp}^*)^2 \frac{a_p}{\mu_p} \right], \quad (11)$$

where P_p^* is the propane pressure on a hydration line, kg/m³.

We can use the Clapeyron-Clausius equation to determine this pressure near the surface of the hydrate

$$P_{p(T)}^* = P_{sp} \exp \left[\frac{r_{gp} \mu_p}{R_\mu} \left(\frac{1}{T_{sp}} - \frac{1}{T_{(R,\tau)}} \right) \right], \quad (12)$$

where r_{gp} is the heat of the “hydrate – gas” phase transition, J/kg; P_{sp}, T_{sp} are the pressure and temperature of the reference point for gas, Pa, K. It is desirable to apply a working point with parameters characteristic for the middle of the working region of pressures and temperatures as a reference point. The heat of the phase transition can be considered as constant at slight changes in temperature (within 0 ÷ +5 °C for propane).

It is necessary to consider a process of heat transfer in a liquid to determine a temperature on the inner surface of a bubble. It occurs due to heat conductivity and convection. The Fourier heat equation is usually used to calculate the heat transfer by heat conduction. We can use an effective coefficient of a heat conductivity to calculate convection. Water can change its thermophysical characteristics (heat conductivity, density, heat capacity) in result of a heat exchange and phase transition processes at the boundary of a bubble, so we will solve the problem as nonlinear. Volumetric sources of heat make possible to take into account the heat of phase transitions.

If one marks a coordinate, which changes the radius of a bubble, as “ x ”, the heat conductivity equation for a sphere with moving boundaries and volumetric sources of heat can be written as [16]

$$\frac{\partial(\rho_r c_r T_{(x,\tau)})}{\partial \tau} = \frac{1}{x^2} \frac{\partial}{\partial x} \left(\lambda_r x^2 \frac{\partial T_{(x,\tau)}}{\partial x} \right) - \dot{R} \frac{\partial(\rho_r c_r T_{(x,\tau)})}{\partial x} + q_{v(x,T)}, \quad (13)$$

where ρ_r is the liquid density, kg/m³; c_r is the heat capacity of a liquid, J/(kg·°C); τ is the time coordinate, s; x is the rate of change in the radius of a bubble, m/s; λ_r is the effective coefficient of a heat conductivity of a liquid, W/(m·°C); q_v is the capacity of volumetric heat sources, W/m³.

The influence of energy of various phase transitions (freezing/thawing, formation/dissociation of gas hydrate) is taken into account with the help of volumetric heat sources. The following formula determines the specific power of volumetric sources or heat losses

$$q_{v(x,T)} = r_{gp} \frac{\partial}{\partial \tau} \left(\frac{\partial m_{gp}}{\partial V_x} \right) + r_r \frac{\partial}{\partial \tau} \left(\frac{\partial m_r}{\partial V_x} \right), \quad (14)$$

where r_r is the heat of the water-ice phase transition, J/kg; m_{gp} is the mass of formed propane hydrate, kg; m_r is the mass of ice formed during water freezing, kg; ∂V is the elementary volume, m³.

Boundary conditions. Taking into account that the heat flow from a gas phase to a liquid (7) has a negative sign, we can write boundary conditions at the surface of a bubble as

$$-\frac{\partial(\lambda_r T)}{\partial x}(R, \tau) = -q. \quad (15)$$

The boundary condition at a considerable distance from a center of a bubble, where the influence of other bubbles becomes equal,

$$-\frac{\partial(\lambda_r T)}{\partial x}(x = \infty, \tau) = 0. \tag{16}$$

Initial time condition

$$T_{(x,\tau=0)} = T_0. \tag{17}$$

The following conditions must be satisfied for hydrate formation:

- the partial pressure of the gas P_p must exceed the minimum pressure of hydration P_{gp}^* at the given temperature, $P_p > P_{gp}^*$;

- the temperature of a liquid $T_{(x,\tau)}$ should be greater than 0 °C, otherwise ice, and not hydrate, will be formed, but it should not exceed the temperature of hydrate formation for given partial pressure, $0 < T_{(x,\tau)} \leq T_{gp}^*$. In the range 0 ÷ +5.5 °C, we can approximate temperature of hydrate formation of propane by the formula, K

$$T_{gp}^* = 245.05 + 26P_p^{0.15}, \tag{18}$$

where P_p is the absolute propane pressure, atm.

We can solve the system of equations (1)–(18) with a use of digital methods, for example, the Runge-Kutta method of 4th order [17, 18]. We determine the mass of hydrate by the removal of heat from the phase transition from the hydrate formation region. For the hydration process (or its dissociation), we assume that the intensity of volumetric heat sources is linearly proportional to the temperature difference between a surface of the phase transition and temperature of the equilibrium state of the hydrate.

5. Results of study of influence of pressure and temperature of a bubble gas medium on hydrate formation processes

Let us consider heat-mass-exchange and hydrodynamic processes at the initial stage of a gas bubble introduction into water [19]. Such processes are technologically characteristic for the formation of hydrate of isobutane [3] and other hydrates [20, 21]. We performed calculations of hydrate formation processes on the surface of bubbles with a diameter of 1 mm with a “winter” propane-butane mixture according to the proposed mathematical model. Output conditions: a gas bubble with a given initial temperature enters water at a temperature of +2.5 °C and a constant absolute pressure of 3.4 bar. We performed a series of calculations of the thermodynamic state of the gas bubble at various initial temperatures of the gas mixture to study the influence of the initial temperature of a gas on the hydration process.

The initial temperature of gases in the bubble can be either higher than the hydration temperature or less. Therefore, we will change a temperature of the gas from the beginning of hydrate formation to the freezing point of water on the surface of the bubble. Fig. 1 shows calculation results.

Row 1 corresponds to the gas temperature of +3 °C, which is 0.5 °C higher than the hydration temperature at this pressure. Further increase of the temperature does not lead to the formation of hydrate for 200 μs. The heating of the gas in the bubble is delayed for a longer period. In general,

a hydration process can only begin with a temperature of +2.5 °C. The higher the initial temperature of a gas, the later a process of hydration formation will begin.

Row 2 corresponds to the initial temperature of 0.5 °C below the hydration temperature. It is seen that the hydrate formation process begins almost immediately and reaches maximum values during the heating of the bubble. We will take the number of hydrates formed at this temperature as a unit for comparison.

Row 3 corresponds to the initial temperature of 0 °C. It is 2.5 °C below the hydrate temperature. Obviously, there is a sharp increase in the amount of hydrate. The quantitative assessment gives a value of 6 times.

Row 4 corresponds to the initial temperature of –5 °C. It is 7.5 °C below the hydration temperature. There is also a sharp increase in the amount of hydrate. The quantitative assessment gives a value of 13 times.

Row 5 corresponds to the initial temperature of –10 °C. It is 12.5 °C lower than the temperature of hydration. Further increase in the amount of hydrate is quite weak. The quantitative assessment gives a value of 15 times. This indicates that further cooling of a gas is ineffective. The reason for the ineffectiveness of further cooling is a freezing of deeper layers of a liquid and an increase in the resistance of a heat transfer. The deterioration of heat dissipation leads to a slow-down in the hydrate formation process.

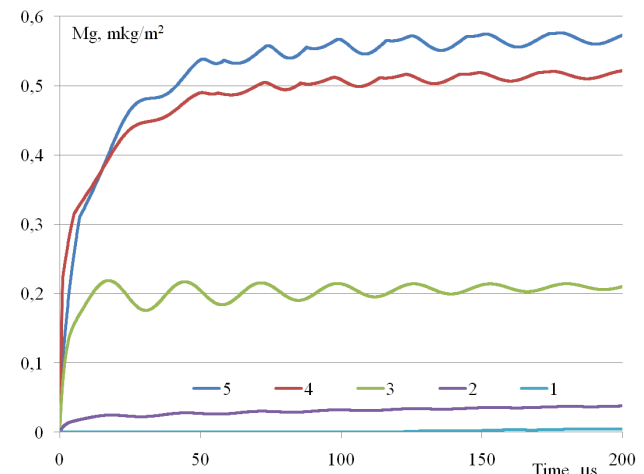


Fig. 1. Hydrate formation at different initial temperature of gas (row 1 – $t=+3$ °C; row 2 – $t=+2$ °C; row 3 – $t=0$ °C; row 4 – $t=-5$ °C; row 5 – $t=-10$ °C)

Fig. 2 shows graphs of temperature of the gas mixture in the middle of the bubble. Line 1 corresponds to the heated gas (to +3 °C). You can see cooling and a small oscillation, which overlaps it. Line 2 corresponds to the initial temperature of +2 °C. We can observe initial heating and small oscillations. Line 3 begins at 0 °C and rises rapidly at 2 °C in 5 μs. Then a fading oscillation process begins. Line 4 shows the process of heating of the medium of the bubble from the initial temperature of –5 °C. Line 5 corresponds to the heating process at the initial temperature of –10 °C.

Fig. 3 shows how the temperature distribution changes in time in liquid layers adjacent to the surface of the bubble. Each layer of the liquid has its thickness, Table 1. Layer 1 contacts the gas medium of the bubble directly, the center of layer 12 is in the liquid at a “depth” of almost 30 % of the radius of the bubble. The thermal wave reached the 6th layer (0.6 % radius) in 200 μs according to Fig. 3.

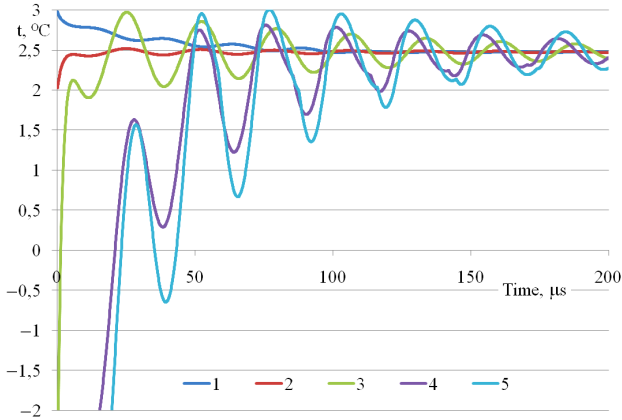


Fig. 2. Gas temperature in a bubble at various initial values
row 1 – $t=+3$ °C; row 2 – $t=+2$ °C; row 3 – $t=0$ °C;
row 4 – $t=-5$ °C; row 5 – $t=-10$ °C

Table 1

Initial parameters of liquid layers		
Order number	Radius of a center of a layer, mm	Average depth, %
1	0.5	0
2	0.500095	0.019
3	0.500286	0.0566
4	0.500668	0.1336
5	0.501428	0.2856
6	0.502943	0.5886
7	0.505945	1.189
8	0.511845	2.369
9	0.523253	4.6506
10	0.544685	8.937
11	0.583110	16.622
12	0.647610	29.522

Fig. 4 illustrates the process of hydrate formation in the liquid layer, which surrounds the oscillating bubble. It can be seen that the hydration process takes place only in the first layer, which has a thickness of only 0.016 % of the radius of the bubble, throughout the entire time interval. The hydrate formation is the most intense during the heating of gas bubbles. Then the process slows down and may be accompanied by partial dissociation during fading oscillations of the bubble.

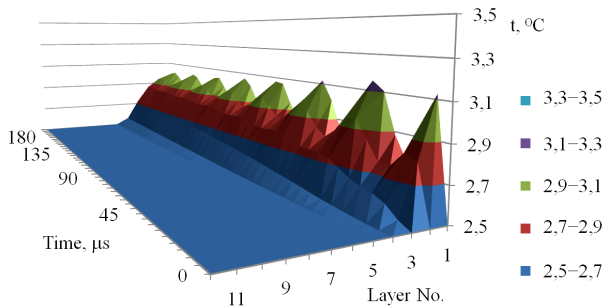


Fig. 3. Temperature of water layers at the initial temperature of 0 °C

Let us analyze the influence of the initial gas pressure on the hydrate formation process. It is known that when

pressure is insufficient, a hydrate formation process will not occur at all. However, what will happen when pressure is raised above the minimum required for a hydration process at a given temperature? We conducted a number of mathematical experiments on a model to clarify this issue. Fig. 5 shows the calculation results for various gas pressures.

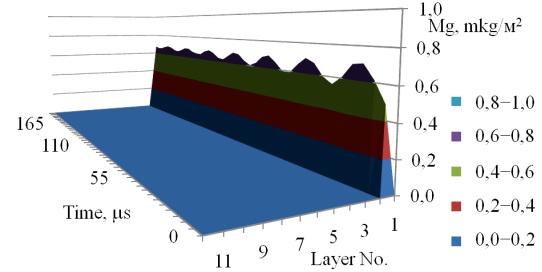


Fig. 4. Hydrate formation at the initial temperature of 0 °C

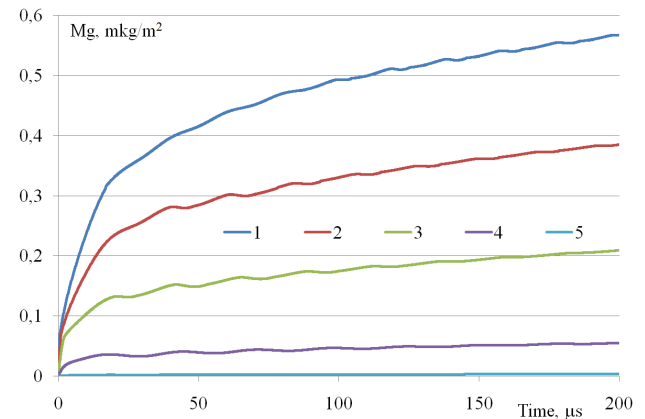


Fig. 5. Hydrate formation at different initial pressures (P bar) 1 – $P=P_{min}+1.5$; 2 – $P=P_{min}+1$; 3 – $P=P_{min}+0.5$;
4 – $P=P_{min}+0.1$; 5 – $P=P_{min}$

We can conclude from Fig. 5 that the amount of formed hydrate increases in proportion to pressure in a gas-water system. Comparing Fig. 5 and 1, it can be seen that when pressure of the oscillation of a bubble increases, the hydrate formation process is less influenced by temperature of a gas. In addition, it is evident that when the temperature of a gas decreases, the hydration process is more intense at the first 60 μ s, and then slows down sharply. In the case of an increase in pressure in the initial region (up to 60 μ s), the process of hydrate formation is slower, but its intensity does not fall in time as quickly as when the temperature of a gas decreases.

Fig. 6 illustrates the temperature regime of the gas medium of the bubble. The temperature of hydrate formation increases with increase in pressure, there is an intense heat emission due to hydrate formation. This leads to the heating of the surface of the bubble and occurs due to the intense heat transfer of the rapid increase in the temperature of a gas in the bubble. We can observe such intensive heating of a gas of the bubble at a short time interval of 20–60 μ s (depends on pressure) only. Then there are fluctuations in the temperature of a gas, which are the result of fading oscillations of the bubble.

Fig. 7–9 present the process of formation of hydrate in liquid layers for various pressures. The first layer was filled with hydrate only by half during the calculated period under

conditions of minimum pressure (Fig. 7). The first layer is filled completely with hydrate, and the second one is filled by about half at an excess pressure of 0.5 bar (Fig. 8). Further increase of excess gas pressure leads to an increase in the thickness of the hydrate layer around the bubble. Fig. 9 shows the first and second layers of the liquid filled with hydrate, and the third is filled by 25 %.

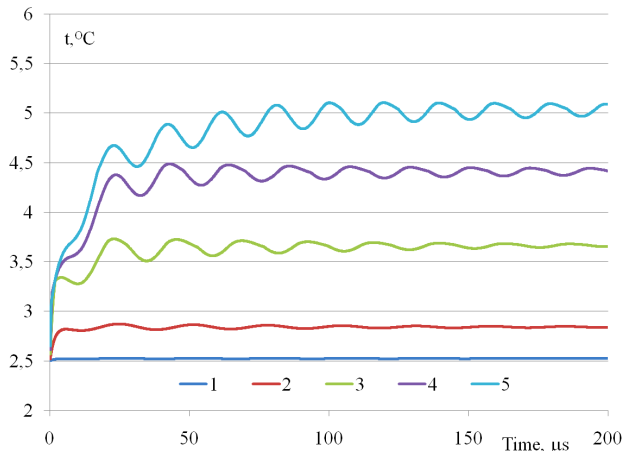


Fig. 6. Gas temperature in a bubble at different initial pressures (P bar) 1 – $P=P_{min}$; 2 – $P=P_{min}+0.1$; 3 – $P=P_{min}+0.5$; 4 – $P=P_{min}+1$; 5 – $P=P_{min}+1.5$ bar

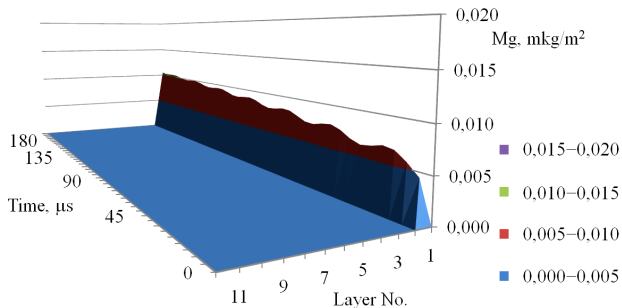


Fig. 7. Formation of hydrate at pressure $P=P_{min}$

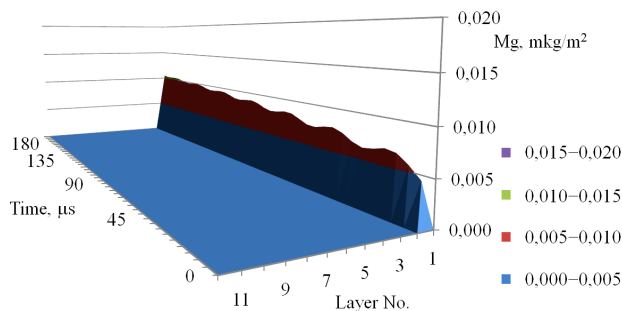


Fig. 8. Formation of hydrate at pressure $P=P_{min}+0.5$ bar

In general, Fig. 7–9 show an increase in the depth of hydrate formation with increase in pressure. However, the depth is very small and is about 0.06 % of the radius of the bubble even for the 3rd layer. Such parameters accord with the formation of microcrystals of hydrates of the thickness of about 1 micron, which are obtained in laboratory conditions. They manifest themselves visually as “turbidity” of water through which bubbles of gas pass. Then the crystals grow together and form a macrostructure of a hydrate.

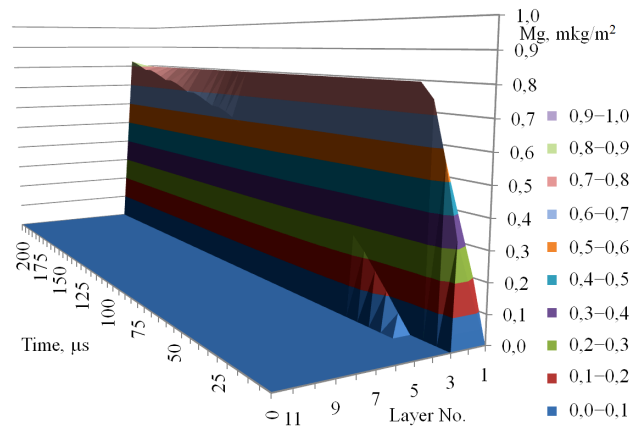


Fig. 9. Formation of hydrate at pressure $P=P_{min}+1.5$ bar

6. Discussion of results of mathematical modeling of hydrate formation on the surface of a gas bubble

Heating of liquid layer bubbles, which are closest to the surface, with simultaneous cooling of the gas occurs firstly at initial temperature of gas +3 °C (Fig. 1). The process of hydrate formation at excess gas temperature does not occur. Calculations show that the hydrate begins to form after sufficient cooling of a gas in a bubble only. This explains a lack of hydrate formation during the first 100 μs. The cooling process is superimposed on fading vibrations of a bubble. Then the temperature stabilizes due to a heat generation caused by hydrate formation. A thermal wave penetrates into water by 2.4 % of a radius of a bubble in 200 μs. The total amount of hydrate is small and the process is very ineffective under such conditions.

When the temperature of a gas in a bubble decreases, the situation changes radically. Fig. 3 shows the temperature regime of liquid layers at the initial temperature of 0 °C. The amount of formed hydrate also increases significantly, Fig. 4. However, as shown in Fig. 4, hydrate is formed only in the first, the thinnest, layer of water. Its thickness is about 0.01 % of the radius of the bubble. In addition, it may partially (dissociate) decompose during oscillations.

It is necessary to cool gas to form a hydrate in deeper layers of the liquid. The results of the calculation at the initial temperature of –5 °C show a rapid “freezing” of the 1st and 2nd layers and a partial freezing of the 3rd layer of the liquid. Moreover, the first and second “freeze” occur in the first 5 microseconds, and the process continues for all 200 microseconds for the 3rd layer. Hydrate formation at the initial temperature of –10 °C proceeds in a similar manner. Moreover, the third layer freezes more intensively than in the previous case, but the amount of hydrate changes little. The reason for this is a deterioration of the drainage of heat from the hydrate formation region.

If to accept the mass of the formed hydrate at a gas temperature of +2 °C per unit, then for different temperatures, a relative amount of hydrate will have the form of dependence shown in Fig. 10. When the initial temperature of a gas mixture increases to +3 °C and the pressure is constant, the hydrate formation process almost stops. There is a uniform increase in a rate of hydrate formation up to temperature of –5 °C. Reduce in the initial temperature of a gas mixture below –5 °C does not lead to a significant acceleration of hydrate formation.

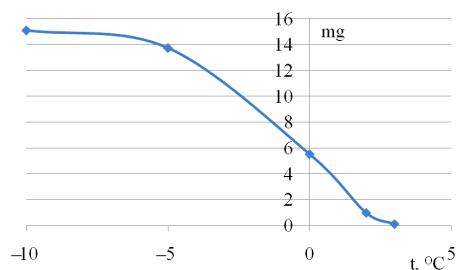


Fig. 10. Influence of gas temperature on hydrate formation

Each gas composition will have an “own” line, which is similar to the curve on Fig. 10, at different pressure values. Their determination is very important for optimization of technological processes and requires additional investigations.

7. Conclusions

1. We supplemented a mathematical model of transition thermodynamic processes of an oscillating gas bubble with a description of diffusion processes on the interphase gas-water surface. In addition, a model takes into account that the composition of a gas mixture may include a hydrate forming component, which can participate in the formation of gas hydrate under certain thermobaric conditions.

2. We performed calculations of transition thermodynamic processes occurring inside and on a surface of an oscillating gas bubble. It was established that the initial temperature of a steam-gas medium of a bubble influences the process of hydrate formation significantly. The most intense hydrate formation takes place at the region of initial heating of a steam-gas medium of a bubble. There is a local increase in the

temperature of liquid during hydrate formation, and after – due to a heat exchange and steam-gas medium of a bubble. We observe the maximum rate of formation of hydrates during a period of gas heating in a bubble. This period has a short duration of $2\div 40 \mu\text{s}$. However, it is the most productive.

We observe oscillations (fading oscillations) of a bubble after the heating period. The starting mechanism for the oscillations is a temperature difference between a gas steam bubble medium and hydration temperature determined by pressure of a medium. The growth of gas temperature leads to an increase in bubble pressure, which results in the process of increasing of its diameter. Hydrate formation occurs during action of oscillations also, but we can observe its dissociation at different moments. This is especially noticeable at not too low gas temperatures ($+3\div 0 \text{ }^\circ\text{C}$).

The oscillations fade gradually and the hydration process is supported by the removal of heat into outer layers of liquid due to the friction in viscous liquid. Since this process is limited to a significant heat transfer resistance of both the liquid and the formed hydrate layers, the rate of formation of hydrates reduces sharply. The performed calculations show that there is an optimal initial gas temperature in a bubble for hydrate formation. This temperature is $-5 \text{ }^\circ\text{C}$ for a pressure of “winter” propane-butane mixture of 3.4 bar.

3. Results of the studies showed that an increase in pressure positively affects the process of hydration, but it is limited to the condensation region of components of the propane-butane mixture. Thus, it is technologically necessary to reduce gas temperature in a bubble and increase pressure to accelerate hydrate formation. The optimal values of pressure and temperature can depend on the composition of gas, the temperature of liquid and the size of bubbles. It is necessary to conduct additional research to determine them.

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