FORMATION OF A GAS HYDRATE DUE TO INJECTION
OF A COLD GAS INTO A POROUS RESERVOIR
PARTLY SATURATED BY WATER

V. Sh. Shagapov,[1] **M. K. Khasanov,**[2]
and N. G. Musakaev[3]

Specific features of formation of gas hydrates due to injection of a gas into a porous medium initially filled by a gas and water are considered. Self-similar solutions of an axisymmetric problem, which describe the distributions of the basic parameters in the reservoir, are constructed. The existence of solutions is demonstrated, which predict gas hydrate formation both on the frontal surface and in the volume zone.

Key words: *gas hydrates, filtration, hydrate formation, self-similar solution, numerical study.*

Introduction. The possibility of gas storage in a hydrate state offers good prospects in industry. Some researchers propose underground gas-hydrate conservation of greenhouse gases, which ensures highly safe storage and does not incur high energy expenses. Other conditions being identical, the gas concentration per unit volume in the hydrate state is much higher than that in the free state [1, 2].

The papers [3–5] that describe the results of mathematical modeling of gas-hydrate decomposition under thermal and depression actions on a porous medium saturated by the gas hydrate and the gas demonstrated the existence of solutions predicting that hydrate decomposition may occur both on the phase-transition surface and in the volume zone.

The specific features of hydrate formation due to gas injection into a porous reservoir initially filled by the gas and water are considered in the present paper in an axisymmetric approximation.

1. Governing Equations. Let the temperatures of the porous medium and the saturating substance (gas, hydrate, or water) be identical. The hydrate is a two-species system with a mass concentration of the gas G. The skeleton of the porous medium, the gas hydrate, and water are incompressible and motionless, the porosity is constant, and the gas is calorically perfect:

$$\rho_{sk}, \rho_h, \rho_l, m = \text{const}, \qquad p = \rho_g R_g T.$$

Here ρ_j $(j = sk, h, l, g)$ are the true densities of the phases, m is the porosity, p is the pressure, T is the temperature, and R_g is the gas constant; the subscripts g, l, h, and sk refer to the parameters of the gas, water, hydrate, and skeleton of the porous medium, respectively.

With allowance for the assumptions made, the equations of conservation of mass for the gas and water in the axisymmetric approximation can be written as

$$\frac{\partial}{\partial t}\left(mS_g\rho_g\right) + \frac{1}{r}\frac{\partial}{\partial r}\left(rS_g m v_g \rho_g\right) = -mG\rho_h\frac{\partial S_h}{\partial t}; \tag{1.1}$$

$$\frac{\partial}{\partial t}\left(mS_l\rho_l\right) = -m(1-G)\rho_h\frac{\partial S_h}{\partial t}; \tag{1.2}$$

[1]Institute of Mechanics, Ufa Scientific Center, Russian Academy of Sciences, Ufa 450025. [2]Sterlitamak State Pedagogical Academy, Sterlitamak 453103. [3]Tyumen' Department of the Khristianovich Institute of Theoretical and Applied Mechanics, Siberian Division, Russian Academy of Sciences, Tyumen', 625026; shagapov@rambler.ru; hasanovmk@mail.ru; musakaev@ikz.ru.

$$S_g + S_l + S_h = 1, \tag{1.3}$$

where S_j $(j = g, l, h)$ is the saturation of pores of the jth phase and v_g is the velocity of the gas phase.

The liquid and gas filtration rates obey the equality $mS_l v_l / (mS_g v_g) = \mu_g k_l / (\mu_l k_g)$ [k_i $(i = l, g)$ are the phase permeability coefficients]. As the dynamic viscosity of the gas μ_g is much lower than the liquid viscosity μ_l, this ratio is usually small (except for the cases where the saturation by water is close to unity). In most cases, therefore, for instance, for the initial saturation of the pores by water $S \leqslant 0.5$ (this is the case considered in the present paper), the assumption on a motionless liquid ($v_l = 0$) is justified.

The gas filtration process obeys the Darcy law

$$mS_g v_g = -\frac{k_g}{\mu_g} \frac{\partial p}{\partial r}. \tag{1.4}$$

Neglecting the barothermal effect, we write the equation for the heat inflow in the form

$$\rho c \frac{\partial T}{\partial t} + \rho_g c_g mS_g v_g \frac{\partial T}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r}\left(r\lambda \frac{\partial T}{\partial x}\right) + m\rho_h L_h \frac{\partial S_h}{\partial t}; \tag{1.5}$$

$$\rho c = (1 - m)\rho_{sk} c_{sk} + m \sum_{j=g,l,h} S_j \rho_j c_j, \qquad \lambda = (1 - m)\lambda_{sk} + m \sum_{j=g,l,h} S_j \lambda_j.$$

Here L_h is the specific heat of hydrate formation, ρc and λ are the specific volume heat and thermal conductivity of the system, and c_j and λ_j are the specific heats and thermal conductivities of the phases, respectively. We assume that the values ρc and λ are constant throughout the reservoir, because the main contribution to these quantities is made by the parameters of the porous medium skeleton.

The dependence of the permeability coefficient of the gas k_g on the saturation by the gas can be defined by the Kozeny formula

$$k_g = k_*(mS_g)^3 / (1 - mS_g)^2 \approx k_0 S_g^3 \qquad (k_0 = k_* m^3).$$

The temperature and pressure in the zone of hydrate formation are related by the condition of phase equilibrium [2]

$$T = T_0 + T_* \ln(p/p_{s0}), \tag{1.6}$$

where T_0 and p_{s0} are the initial temperature of the system and the corresponding equilibrium pressure, and T_* is an empirical parameter depending on the type of the gas hydrate.

In the general case, three typical zones can arise in the porous reservoir in the course of hydrate formation. In the zone near the well (near zone), the pores are filled by the gas and hydrate. Gas hydrate formation occurs in the intermediate zone; hence, the pores there are filled by the gas, water, and hydrate. In the zone at a significant distance from the well (far zone), the pores are filled by the gas and water. The conditions of conservation of mass and heat have to be satisfied on the boundaries of these zones:

$$\left[m(S_h\rho_h(1 - G) + S_l\rho_l)\dot{r}_{(i)}\right] = 0, \qquad \left[m(\rho_g S_g(v_g - \dot{r}_{(i)}) - \rho_h S_h G\dot{r}_{(i)})\right] = 0,$$

$$\left[\lambda \frac{\partial T}{\partial r}\right] = \left[m\rho_h L_h S_h \dot{r}_{(i)}\right]. \tag{1.7}$$

Here $[f]$ is the jump of the quantity f on the boundary $r_{(i)}$ $(i = s, m)$ between the zones, $\dot{r}_{(i)}$ is the velocity of motion of this boundary, $r_{(s)}$ is the boundary between the near and intermediate zones, and $r_{(m)}$ is the boundary between the intermediate and far zones. The temperature and pressure on these boundaries are assumed to be continuous.

It should be noted that the intensity of hydrate formation in the equilibrium scheme used (both on the frontal surfaces and in volume zones) is bounded by removal of latent heat of hydrate formation.

According to the modern concepts [6], formation of hydrate particles is accompanied by nonequilibrium processes caused by diffusion of the hydrate-forming gas toward the water–hydrate contact surface through water and hydrate layers. Assuming the characteristic thicknesses of such layers to be of the order of the pore channel size $\sqrt{k/m}$, we can estimate the characteristic times t_D of relaxation of diffusion nonequilibrium as $t_D \simeq k/(mD)$, where D is the diffusion coefficient. As compared with times of interest for the present problem, these characteristic times are usually very small.

From the equation of continuity for water (1.2), we obtain

$$\rho_l(S_l - S_{l0}) + (1 - G)\rho_h S_h = 0 \tag{1.8}$$

(S_{l0} is the initial saturation by water). Thus, with allowance for Eq. (1.3), we have

$$S_l = S_{l0} - (\rho_h/\rho_l)(1 - G)S_h, \qquad S_g = 1 - S_{l0} - (1 - (\rho_h/\rho_l)(1 - G))S_h.$$

In the present axisymmetric problem on gas injection into a horizontal porous reservoir, we assume that this reservoir is saturated by the gas and water whose pressures p_0 and temperatures T_0 in the initial state correspond to the thermodynamic conditions of their existence in the free state ($p_0 \leqslant p_{s0}$) and are identical throughout the reservoir at the initial time:

$$t = 0: \qquad T = T_0, \quad p = p_0 \quad (r \geqslant r_w). \tag{1.9}$$

Let the gas (the same as the initial gas) with a constant temperature T_w be injected with a permanent mass flow rate Q_g through a well opening the reservoir throughout its entire thickness. Owing to gas injection, a zone saturated by the gas and hydrate is formed near the well. We assume that the influence of the well size on the characteristics of the process is insignificant if the times of gas injection are rather large, when the size of this zone is much greater than the well radius ($r_{(s)} \gg r_w$). Then, with allowance for the Darcy law and the equation of state of the gas, the conditions on the well boundary have the form

$$r = r_w: \qquad -\frac{k_g \pi}{\mu_g R_g T_w}\left(r \frac{\partial p^2}{\partial r}\right) = Q_g, \quad T = T_w \quad (r_w \to 0, \ t > 0). \tag{1.10}$$

The problem formulated has a self-similar solution.

2. Solution with the Frontal Surface of Phase Transitions. In this case, two characteristic zones are formed. In the zone near the well, water completely transforms to the gas-hydrate state; hence, the pores contain only the gas and gas hydrate. In the second (far) zone, the pores of the reservoir are filled by the gas and water. Hence, gas-hydrate formation occurs on the frontal surface between these zones only, and there is no intermediate zone.

By introducing the self-similar variable

$$\xi = r/\sqrt{\alpha^{(T)}t}$$

[$\alpha^{(T)} = \lambda/(\rho c)$ is the thermal diffusivity of the reservoir] and taking into account Eqs. (1.1)–(1.5), we can write the equations of thermal diffusivity and piezoconductivity as

$$-\frac{1}{2}\xi \frac{dT_{(i)}}{d\xi} = \frac{1}{2}\frac{\mathrm{Pe}_{(i)}}{p_0^2}\frac{dp_{(i)}^2}{d\xi}\frac{dT_{(i)}}{d\xi} + \frac{1}{\xi}\frac{d}{d\xi}\left(\xi \frac{dT_{(i)}}{d\xi}\right),$$

$$-\xi \frac{dp_{(i)}^2}{d\xi} = 2\eta_{(i)}\frac{1}{\xi}\frac{d}{d\xi}\left(\xi \frac{dp_{(i)}^2}{d\xi}\right), \tag{2.1}$$

where

$$\eta_{(i)} = \frac{\alpha_{(i)}^{(p)}}{\alpha^{(T)}}, \qquad \alpha_{(i)}^{(p)} = \frac{k_{(i)}p_0}{mS_{g(i)}\mu_g}, \qquad \mathrm{Pe}_{(i)} = \frac{\rho_{g0}c_g}{\lambda}\frac{k_{(i)}p_0}{\mu_g}, \qquad k_{(i)} = k_0 S_{g(i)}^3;$$

the subscripts in brackets $i = 1, 2$ refer to the parameters of the first and second zones, respectively. Note that the piezoconductivity equation is obtained by Leibenzon's method of linearization [7].

On the interface between the near and far zones, there occurs a jump of the saturation by the hydrate from $S_h^- = S_{h(1)}$ to $S_h^+ = 0$. The saturation by the hydrate in the first zone $S_{h(1)}$ is determined from condition (1.8):

$$S_{h(1)} = \rho_l S_{l0}/(\rho_h(1 - G)).$$

The pressure and temperature on the interface between these zones are related by the condition of phase equilibrium (1.6).

Using Eqs. (1.7), we write the system of equations for determining the self-similar coordinate $\xi_{(s)}$ of the phase-transition boundary and the values of parameters on this boundary as

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$$\frac{dT_{(1)}}{d\xi} - \frac{dT_{(2)}}{d\xi} = \frac{\Delta T \, S_{h(1)}}{2} \, \xi_{(s)}, \qquad k_{(2)} \frac{dp_{(2)}^2}{d\xi} - k_{(1)} \frac{dp_{(1)}^2}{d\xi} = K S_{h(1)} \xi_{(s)}, \tag{2.2}$$

where

$$\Delta T = m \rho_h L_h / (\rho c), \qquad K = m \mu_g \alpha^{(T)} p_0 (\rho_h G / \rho_{g0} + \rho_h (1 - G) / \rho_l - 1).$$

By integrating Eqs. (2.1) and taking into account the initial and boundary conditions (1.9) and (1.10) for pressure and temperature in each zone, we obtain

$$p_{(1)}^2 = p_{(s)}^2 + \frac{Q_g \mu_g R_g T_w}{\pi k_{(1)}} \int\limits_{\xi}^{\xi_{(s)}} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4\eta_{(1)}} \right) d\xi,$$

$$T_{(1)} = T_{(s)} + (T_w - T_{(s)}) \int\limits_{\xi}^{\xi_{(s)}} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(1)}^2 \right) d\xi \Big/ \int\limits_{0}^{\xi_{(s)}} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(1)}^2 \right) d\xi; \tag{2.3}$$

$$p_{(2)}^2 = p_0^2 + (p_{(s)}^2 - p_0^2) \int\limits_{\xi}^{\infty} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4\eta_{(2)}} \right) d\xi \Big/ \int\limits_{\xi_{(s)}}^{\infty} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4\eta_{(2)}} \right) d\xi,$$

$$T_{(2)} = T_0 + (T_{(s)} - T_0) \int\limits_{\xi}^{\infty} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(2)}^2 \right) d\xi \Big/ \int\limits_{\xi_{(s)}}^{\infty} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(2)}^2 \right) d\xi. \tag{2.4}$$

After substitution of solutions (2.3), (2.4) into the system of the boundary conditions (2.2), the latter acquires the form

$$k_{(2)}(p_0^2 - p_{(s)}^2) \exp\left(-\frac{\xi_{(s)}^2}{4\eta_{(2)}} \right) \Big/ \int\limits_{\xi_{(s)}}^{\infty} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4\eta_{(2)}} \right) d\xi + \frac{Q_g \mu_g R_g T_w}{\pi} \, \exp\left(-\frac{\xi_{(s)}^2}{4\eta_{(1)}} \right) = K S_{h(1)} \xi_{(s)}^2; \tag{2.5}$$

$$(T_{(s)} - T_w) \exp\left(-\frac{\xi_{(s)}^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(s)}^2 \right) \Big/ \int\limits_{0}^{\xi_{(s)}} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(1)}^2 \right) d\xi$$

$$-(T_0 - T_{(s)}) \exp\left(-\frac{\xi_{(s)}^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(s)}^2 \right) \Big/ \int\limits_{\xi_{(s)}}^{\infty} \frac{1}{\xi} \, \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(2)}^2 \right) d\xi = \frac{\Delta T \, S_{h(1)}}{2} \, \xi_{(s)}^2. \tag{2.6}$$

System (2.5), (2.6) can be resolved as follows. Expressing the quantity $p_{(s)}$ explicitly from Eq. (2.5), substituting it into Eq. (2.6), and taking into account condition (1.6), we obtain a transcendental equation with one unknown $\xi_{(s)}$. Solving the resultant equation (e.g., by the method of dichotomy), we find the value of $\xi_{(s)}$ and then the pressure and temperature distributions in the first and second zones, including the values of these parameters on the interface between the zones.

Figure 1a shows the temperature and pressure distributions for injection of the gas (methane) with a mass flow rate $Q_g = 0.02$ kg/(m·sec) and temperature $T_w = 278$ K into a reservoir with an initial pressure $p_0 = 4$ MPa and initial saturation by water $S_{l0} = 0.2$. Curve 2 in Fig. 1a shows the distribution of the equilibrium temperature corresponding to the pressure distribution obtained.

It is seen in Fig. 1a that the reservoir temperature ahead of the hydrate-formation front is lower than the equilibrium temperature, and the reservoir temperature behind the front is higher than the equilibrium temperature, which does not contradict physical principles. In this case, therefore, we can speak about the existence of a solution with the frontal surface of hydrate formation.

Figure 1b shows the temperature and pressure distributions for injection of the gas with a mass flow rate $Q_g = 0.1$ kg/(m·sec) and temperature $T_w = 278$ K. It is seen that the reservoir temperature behind the front
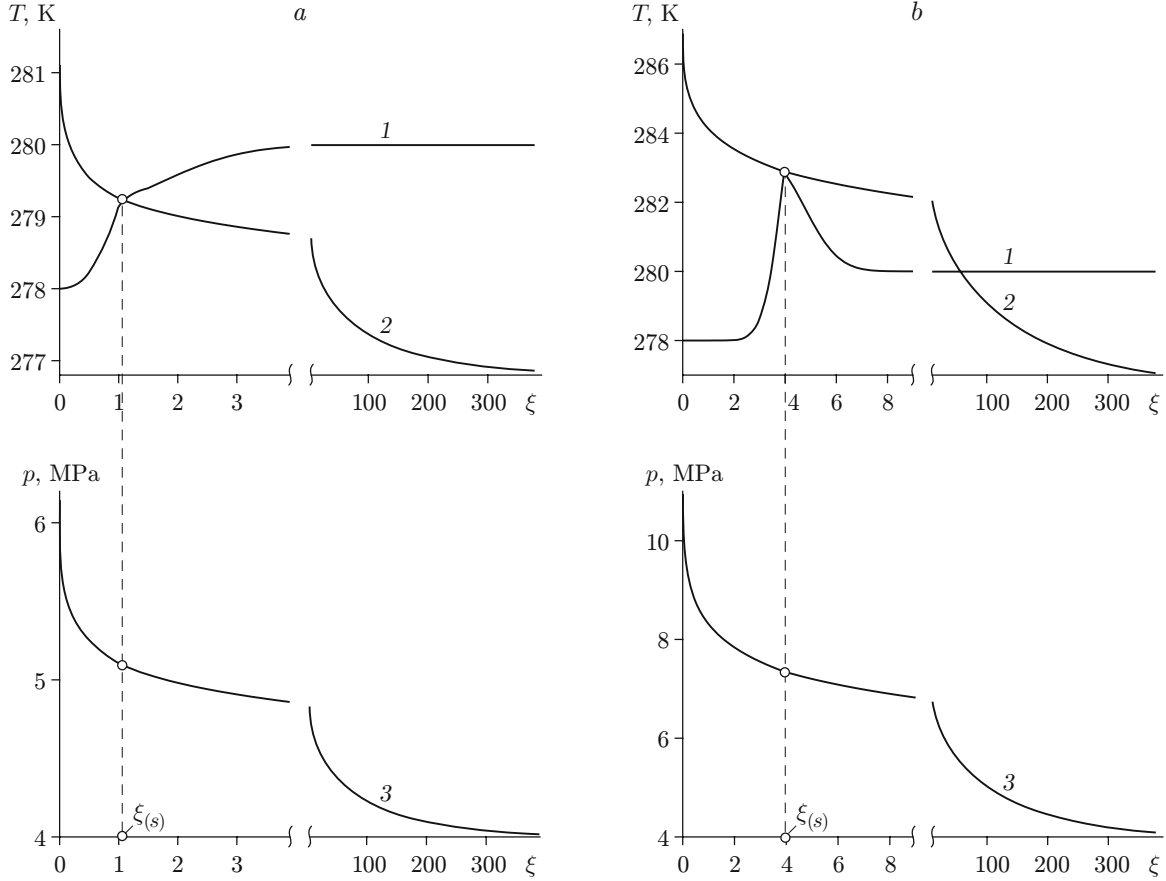
Fig. 1. Distributions of the reservoir temperature (1), equilibrium temperature (2), and pressure (3) for $T_w = 278$ K, $p_0 = 4$ MPa, $S_{l0} = 0.2$, $m = 0.1$, $G = 0.12$, $T_0 = 280$ K, $T_* = 10$ K, $p_{s0} = 5.5$ MPa, $k_0 = 10^{-14}$ m^2, $\rho_{sk} = 2 \cdot 10^3$ kg/m^3, $\rho_h = 900$ kg/m^3, $\rho_l = 1000$ kg/m^3, $R_g = 520$ J/(K·kg), $\rho c = 2.5 \cdot 10^6$ J/(K·m^3), $\lambda = 2$ W/(m·K), $\mu_g = 10^{-5}$ kg/(m·sec), $L_h = 5 \cdot 10^5$ J/kg, $c_{sk} = 1000$ J/(K·kg), $c_h = 900$ J/(K·kg), $c_l = 4200$ J/(K·kg), $c_g = 1560$ J/(K·kg), and different mass flow rates of the gas: $Q_g = 0.02$ (a) and 0.1 kg/(m·sec) (b).

of hydrate formation is lower than the equilibrium temperature (curve 2 in Fig. 1b), i.e., water supercooling is observed in this zone. Thus, for the mass flow rate used, the model of hydrate formation on the frontal surface does not allow a physically noncontradictory solution to be constructed. To eliminate this contradiction, it is necessary to introduce an extended zone of hydrate formation.

The volume zone of hydrate formation arises if the following condition is satisfied on the phase-transition boundary ($\xi = \xi_{(s)}$):

$$\frac{dT_{(2)}}{d\xi} < \frac{dT_{(2)s}}{d\xi}$$

[$T_{(2)s}$ is the temperature of hydrate formation corresponding to the pressure $p_{(2)}$]. It follows from Eq. (1.6) that

$$\frac{dT_{(2)s}}{d\xi} = \frac{T_*}{2p_{(s)}^2} \frac{dp_{(2)}^2}{d\xi}.$$

Using the boundary equations (2.2), we obtain the condition of the onset of an extended zone

$$\frac{dT_{(1)}}{d\xi} - \frac{\Delta T S_{h(1)}}{2} \xi_{(s)} < \frac{T_*}{2k_{(2)}p_{(s)}^2}\left(k_{(1)} \frac{dp_{(1)}^2}{d\xi} + KS_{h(1)}\xi_{(s)}\right),$$

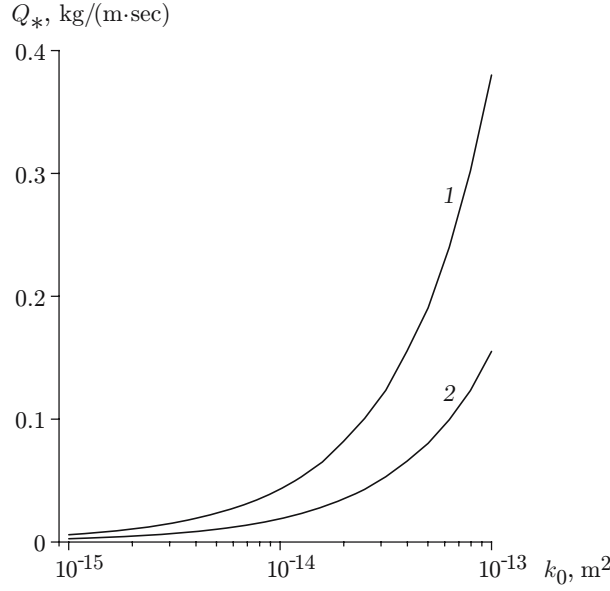which, with allowance for solutions (2.3), acquires the form

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Fig. 2. Critical mass flow rate of the gas Q_* versus the permeability coefficient k_0 for different values of the initial saturation of the reservoir by water: $S_{l0} = 0.2$ (1) and 0.4 (2).

$$(T_{(s)} - T_w) \exp\left(-\frac{\xi_{(s)}^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2} p_{(s)}^2\right) \Big/ \int_0^{\xi_{(s)}} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2} p_{(1)}^2\right) d\xi - \frac{\Delta T S_{h(1)}}{2} \xi_{(s)}^2$$

$$< \frac{T_*}{2k_{(2)}p_{(s)}^2}\left(-\frac{Q_g \mu_g R_g T_w}{\pi} \exp\left(-\frac{\xi_{(s)}^2}{4\eta_{(1)}}\right) + K S_{h(1)} \xi_{(s)}^2\right). \tag{2.7}$$

Numerical experiments were performed in wide ranges of parameters with the use of inequality (2.7) and system (2.5), (2.6). The results of numerical calculations allow us to conclude that there is a critical mass flow rate of the gas Q_* for each value of permeability with the volume zone of hydrate formation appearing if this critical value is exceeded. This dependence is plotted in Fig. 2 for two values of the initial saturation of the reservoir by water.

3. Solution with a Volume Zone of Phase Transitions. If hydrate formation occurs in a volume zone, there appear three typical zones in the reservoir: the near (first) zone where the pores are filled by the gas and hydrate, the intermediate (second) zone where the gas, water, and hydrate are simultaneously present, and the far (third) zone filled by the gas and water. Hydrate formation occurs in the intermediate zone. Correspondingly, two surfaces appear: the surface between the far and intermediate zones, where the process of hydrate formation begins, and the surface between the near and intermediate zones, where this process is finished.

For the near and far zones, the equations of thermal diffusivity and piezoconductivity in self-similar variables can be presented in the form (2.1).

Using Eqs. (1.1)–(1.5) in the intermediate zone, we obtain

$$-\xi \frac{dp_{(2)}^2}{d\xi} = 2\eta_{(2)} \frac{1}{\xi} \frac{d}{d\xi}\left(\xi \frac{dp_{(2)}^2}{d\xi}\right) + 2R_h p_{(2)}^2 \xi \frac{dS_{h(2)}}{d\xi}; \tag{3.1}$$

$$-\xi \frac{dT_{(2)}}{d\xi} = \frac{\mathrm{Pe}_{(2)}}{p_0^2} \frac{dp_{(2)}^2}{d\xi} \frac{dT_{(2)}}{d\xi} + \frac{2}{\xi} \frac{d}{d\xi}\left(\xi \frac{dT_{(2)}}{d\xi}\right) - \Delta T \xi \frac{dS_{h(2)}}{d\xi}. \tag{3.2}$$

In Eqs. (3.1) and (3.2),

$$\eta_{(2)} = \frac{k_{(2)}p_0}{\mu_g m S_{g(2)} \alpha^{(T)}}, \qquad \mathrm{Pe}_{(2)} = \frac{\rho_{g0} c_g}{\lambda} \frac{k_{(2)}p_0}{\mu_g}, \qquad R_h = \frac{\rho_h G}{\rho_{g0} S_{g(2)}}.$$

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Hereinafter, the saturation by the gas and permeability in the second zone are assumed to be constant and equal to their values in the third zone:

$$S_{g(2)} = S_{g(3)} = 1 - S_{l0}, \qquad k_{(2)} = k_{(3)} = k_0(1 - S_{l0})^3.$$

In addition, the temperature and pressure in the intermediate zone are related by the phase equilibrium condition

$$T_{(2)} = T_0 + T_* \ln (p_{(2)}/p_{s0}). \tag{3.3}$$

It follows from Eq. (3.3) that

$$\frac{dT_{(2)}}{d\xi} = \frac{T_*}{2p_{(2)}^2} \frac{dp_{(2)}^2}{d\xi}. \tag{3.4}$$

Substituting Eq. (3.4) into Eq. (3.2), we obtain

$$-\xi \frac{dp_{(2)}^2}{d\xi} = \frac{\mathrm{Pe}_{(2)}}{p_0^2} \Big(\frac{dp_{(2)}^2}{d\xi}\Big)^2 + \frac{2}{\xi} \frac{d}{d\xi}\Big(\xi \frac{dp_{(2)}^2}{d\xi}\Big) - 2\frac{\Delta T}{T_*} p_{(2)}^2 \xi \frac{dS_{h(2)}}{d\xi}. \tag{3.5}$$

Expressing the derivative $dS_{h(2)}/d\xi$ from Eq. (3.1) and substituting this derivative into Eq. (3.5), we obtain

$$-\frac{R_h T_* + \Delta T}{2R_h T_*} \xi \frac{dp_{(2)}^2}{d\xi} = \frac{\mathrm{Pe}_{(2)}}{2p_0^2} \Big(\frac{dp_{(2)}^2}{d\xi}\Big)^2 + \frac{1}{\xi} \frac{T_* R_h + \Delta T \eta_{(2)}}{T_* R_h} \frac{d}{d\xi}\Big(\xi \frac{dp_{(2)}^2}{d\xi}\Big). \tag{3.6}$$

The second term in the right side of Eq. (3.6) can be presented in the form of two terms as

$$-\frac{R_h T_* + \Delta T}{2R_h T_*} \xi \frac{dp_{(2)}^2}{d\xi} = \frac{\mathrm{Pe}_{(2)}}{2p_0^2} \Big(\frac{dp_{(2)}^2}{d\xi}\Big)^2 + \frac{T_* R_h + \Delta T \eta_{(2)}}{T_* R_h} \frac{d}{d\xi}\Big(\frac{dp_{(2)}^2}{d\xi}\Big) + \frac{T_* R_h + \Delta T \eta_{(2)}}{T_* R_h} \frac{1}{\xi} \frac{dp_{(2)}^2}{d\xi}. \tag{3.7}$$

We write the relation between the first and second terms in the right side of Eq. (3.7) in the form

$$\chi = \frac{\mathrm{Pe}_{(2)} \Delta p_{(2)}^2 T_* R_h}{2p_0^2(\Delta T \eta_{(2)} + T_* R_h)},$$

where $\Delta p_{(2)}^2$ is the characteristic difference in pressure $p_{(2)}^2$ in the second zone.

As $\chi \ll 1$ in most cases of practical importance, Eq. (3.6) can be presented as

$$-\frac{d}{d\xi}\Big(\xi \frac{dp_{(2)}^2}{d\xi}\Big) = \frac{1}{2\eta_*} \xi^2 \frac{dp_{(2)}^2}{d\xi}, \tag{3.8}$$

where $\eta_* = (\Delta T \eta_{(2)} + R_h T_*)/(\Delta T + R_h T_*)$. With allowance for Eq. (3.8), formula (3.1) yields the first-order differential equation relating the saturation by the hydrate and the pressure in the second zone:

$$\frac{\eta_{(2)} - \eta_*}{\eta_*} \xi \frac{dp_{(2)}^2}{d\xi} = 2R_h p_{(2)}^2 \xi \frac{dS_{h(2)}}{d\xi}. \tag{3.9}$$

On the surface $r = r_{(s)}$ separating the near and intermediate zones (on the first boundary), the saturation by the hydrate increases in a jumplike manner from $S_h^- = S_{h(1)}$ to $S_h^+ = S_{h(s)}$. Then, using relations (1.7) and condition (3.3), we write the following system of equations for finding the coordinate of the first boundary $\xi_{(s)}$ and the values of parameters on this boundary:

$$k_{(2)} \frac{dp_{(2)}^2}{d\xi} - k_{(1)} \frac{dp_{(1)}^2}{d\xi} = K(S_{h(1)} - S_{h(s)})\xi_{(s)},$$

$$\frac{dT_{(1)}}{d\xi} - \frac{dT_{(2)}}{d\xi} = \frac{\Delta T}{2} (S_{h(1)} - S_{h(s)})\xi_{(s)}, \qquad \frac{dT_{(2)}}{d\xi} = \frac{T_*}{2p_{(s)}^2} \frac{dp_{(2)}^2}{d\xi}. \tag{3.10}$$

On the surface $r = r_{(m)}$ separating the far and intermediate zones (on the second boundary), the saturation by the hydrate $S_{h(m)}$ is assumed to be continuous and equal to zero:

$$S_{h(m)}^- = S_{h(m)}^+ = 0. \tag{3.11}$$

Within the framework of the model considered, any jump in the saturation by the hydrate on the second boundary results in formation of a zone in the third zone with the reservoir temperature lower than the hydrate

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formation temperature. Thus, condition (3.11) is the only possible solution for the saturation by the hydrate on the second boundary, which ensures a thermodynamically noncontradictory solution in the third zone.

With allowance for relations (1.7) and condition (3.3), the system of equations for the coordinate of the second boundary $\xi_{(m)}$ and the values of parameters on this boundary takes the form

$$\frac{dp_{(2)}^2}{d\xi} = \frac{dp_{(3)}^2}{d\xi}, \qquad \frac{dT_{(2)}}{d\xi} = \frac{dT_{(3)}}{d\xi}, \qquad \frac{dT_{(2)}}{d\xi} = \frac{T_*}{2p_{(m)}^2} \frac{dp_{(2)}^2}{d\xi}. \tag{3.12}$$

The distributions of pressure and temperature in the near zone are described by solutions that coincide with solutions (2.3).

Integrating Eq. (3.8), we obtain the pressure distribution in the intermediate zone

$$p_{(2)}^2 = p_{(m)}^2 + (p_{(s)}^2 - p_{(m)}^2) \int_{\xi}^{\xi_{(m)}} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4\eta_*}\right) d\xi \Big/ \int_{\xi_{(s)}}^{\xi_{(m)}} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4\eta_*}\right) d\xi. \tag{3.13}$$

The distribution of the temperature T_2 in this zone corresponding to the pressure distribution (3.13) is related to the latter by the phase equilibrium condition (3.3).

Integrating Eq. (3.9) and taking into account condition (3.11), we obtain the expression for the distribution of the saturation by the hydrate in the intermediate zone

$$S_{h(2)} = \frac{\eta_{(2)} - \eta_*}{2R_h\eta_*} \ln \frac{p_{(2)}^2}{p_{(m)}^2},$$

from which we find the saturation by the hydrate on the first boundary (on the side of the intermediate zone):

$$S_{h(s)} = \frac{\eta_{(2)} - \eta_*}{2R_h\eta_*} \ln \frac{p_{(s)}^2}{p_{(m)}^2}. \tag{3.14}$$

For the far zone, we have

$$p_{(3)}^2 = p_0^2 + (p_{(m)}^2 - p_0^2) \int_{\xi}^{\infty} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4\eta_{(3)}}\right) d\xi \Big/ \int_{\xi_{(m)}}^{\infty} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4\eta_{(3)}}\right) d\xi,$$

$$T_{(3)} = T_0 + (T_{(m)} - T_0) \int_{\xi}^{\infty} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4} - \frac{\mathrm{Pe}_{(3)}}{2p_0^2} p_{(3)}^2\right) d\xi \Big/ \int_{\xi_{(m)}}^{\infty} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4} - \frac{\mathrm{Pe}_{(3)}}{2p_0^2} p_{(3)}^2\right) d\xi.$$

Substituting the solutions obtained for the pressure and temperature distributions in the first and second zones into Eq. (3.10), we write the system of equations for the parameters on the first boundary in the following form:

$$k_{(2)}(p_{(m)}^2 - p_{(s)}^2) \exp\left(-\frac{\xi_{(s)}^2}{4\eta_*}\right) \Big/ \int_{\xi_{(s)}}^{\xi_{(m)}} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4\eta_*}\right) d\xi + \frac{Q_g\mu_g R_g T_w}{\pi} \exp\left(-\frac{\xi_{(s)}^2}{4\eta_{(1)}}\right) = K(S_{h(1)} - S_{h(s)})\xi_{(s)}^2; \tag{3.15}$$

$$(T_{(s)} - T_w) \exp\left(-\frac{\xi_{(s)}^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2} p_{(s)}^2\right) \Big/ \int_{0}^{\xi_{(s)}} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2} p_{(1)}^2\right) d\xi$$

$$-\frac{T_*}{2p_{(s)}^2} (p_{(m)}^2 - p_{(s)}^2) \exp\left(-\frac{\xi_{(s)}^2}{4\eta_*}\right) \Big/ \int_{\xi_{(s)}}^{\xi_{(m)}} \frac{1}{\xi} \exp\left(-\frac{\xi^2}{4\eta_*}\right) d\xi = \frac{\Delta T}{2} (S_{h(1)} - S_{h(s)})\xi_{(s)}^2. \tag{3.16}$$

Similarly, substituting the solutions obtained for the pressure and temperature distributions in the second and third zones into Eq. (3.12), we obtain the system of equations for the second boundary:

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$$(p_{(m)}^2 - p_{(s)}^2)\exp\left(-\frac{\xi_{(m)}^2}{4\eta_*}\right)\Bigg/ \int_{\xi_{(s)}}^{\xi_{(m)}} \frac{1}{\xi}\exp\left(-\frac{\xi^2}{4\eta_*}\right)d\xi = (p_0^2 - p_{(m)}^2)\exp\left(-\frac{\xi_{(m)}^2}{4\eta_{(3)}}\right)\Bigg/ \int_{\xi_{(m)}}^{\infty} \frac{1}{\xi}\exp\left(-\frac{\xi^2}{4\eta_{(3)}}\right)d\xi; \qquad (3.17)$$

$$\frac{T_*}{2p_{(m)}^2}(p_{(m)}^2 - p_{(s)}^2)\exp\left(-\frac{\xi_{(m)}^2}{4\eta_*}\right)\Bigg/ \int_{\xi_{(s)}}^{\xi_{(m)}} \frac{1}{\xi}\exp\left(-\frac{\xi^2}{4\eta_*}\right)d\xi$$

$$= (T_0 - T_{(m)})\exp\left(-\frac{\xi_{(m)}^2}{4} - \frac{\mathrm{Pe}_{(3)}}{2p_0^2}p_{(m)}^2\right)\Bigg/ \int_{\xi_{(m)}}^{\infty} \frac{1}{\xi}\exp\left(-\frac{\xi^2}{4} - \frac{\mathrm{Pe}_{(3)}}{2p_0^2}p_{(3)}^2\right)d\xi. \qquad (3.18)$$

The temperature and pressure on these boundaries are related by the phase equilibrium conditions

$$T_{(s)} = T_0 + T_* \ln(p_{(s)}/p_{s0}), \qquad T_{(m)} = T_0 + T_* \ln(p_{(m)}/p_{s0}).$$

The system of the boundary conditions (3.15)–(3.18) is solved by the following procedure. First we define the zeroth approximation of the sought quantities on the first boundary (the values of the parameters on the hydrate formation front calculated by the frontal model were taken as such an approximation). Then, expressing the value of $p_{(m)}$ from Eq. (3.17) and substituting it into Eq. (3.18), we obtain a transcendental equation with one unknown $\xi_{(m)}$. Solving this equation (e.g., by the method of dichotomy), we find the value of $\xi_{(m)}$ and then $p_{(m)}$. After that, knowing the values of parameters on the second boundary, we find the value of $p_{(s)}$ from Eq. (3.15) and substitute this value into Eq. (3.16). We obtain a transcendental equation with one unknown $\xi_{(s)}$; by solving this equation, we determine a new approximate value of the coordinate of the first boundary $\xi_{(s)}$, and then a new approximate value of the pressure $p_{(s)}$. After cyclic repetitions of this iterative procedure, we obtain a sequence of approximate values converging to the sought values of the boundary parameters.

Figure 3 shows the distributions of temperature and saturation by the hydrate for a mass flow rate close to the critical value Q_* at which the frontal surface of hydrate formation transforms to a volume zone. It follows from Fig. 3 that there appears an intermediate zone as the critical value of the mass flow rate is exceeded, and the length of this intermediate zone increases with a further increase in the flow rate of the gas. It also follows from Fig. 3 that the main part of water transforms to the gas hydrate on the frontal surface, and the temperature in the zone of hydrate formation is only slightly higher than the initial temperature of the reservoir.

Figure 4 shows the distributions of pressure, temperature, and saturation by the hydrate for the case of high-intensity injection of the gas. It is seen from Fig. 4 that the temperature in the hydrate formation zone is substantially higher than the initial temperature of the reservoir if the gas is injected with high mass flow rates. This is caused by the fact that the pressure in the intermediate zone is much higher than the equilibrium pressure p_{s0} corresponding to the initial temperature T_0. Hence, injection of a cold ($T_w < T_0$) gas into the reservoir leads to its heating, and the degree of heating increases with increasing mass flow rate of the injected gas. In addition, it follows from Fig. 4 that an increase in the mass flow rate of the gas substantially increases the length of the intermediate zone and the fraction of hydrates formed in this zone (as compared with the amount of hydrates formed on the frontal surface separating the near and intermediate zones). Thus, as the mass flow rate of the gas increases, the process of hydrate formation in the volume zone becomes more and more different from the above-considered formation of hydrates on the frontal surface.

It was demonstrated in Sec. 2 that an extended zone of hydrate formation arises if inequality (2.7) is valid. Let us consider the limit case

$$(T_{(s)} - T_w)\exp\left(-\frac{\xi_{(s)}^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2}p_{(s)}^2\right)\Bigg/ \int_0^{\xi_{(s)}} \frac{1}{\xi}\exp\left(-\frac{\xi^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2}p_{(1)}^2\right)d\xi - \frac{\Delta T\, S_{h(1)}}{2}\xi_{(s)}^2$$

$$= \frac{T_*}{2k_{(2)}p_{(s)}^2}\left(-\frac{Q_g\mu_g R_g T_w}{\pi}\exp\left(-\frac{\xi_{(s)}^2}{4\eta_{(1)}}\right) + K S_{h(1)}\xi_{(s)}^2\right). \qquad (3.19)$$
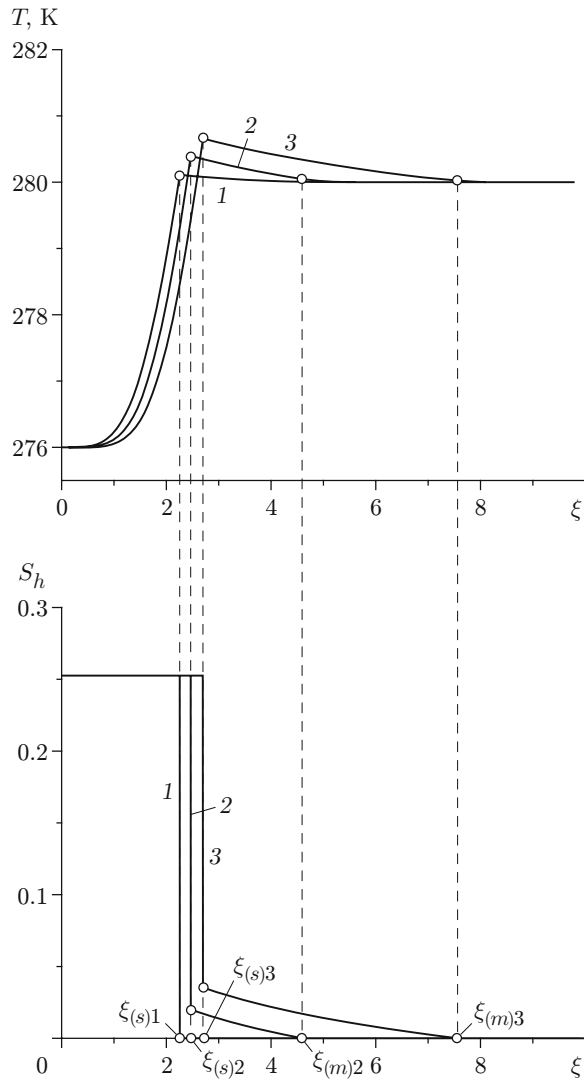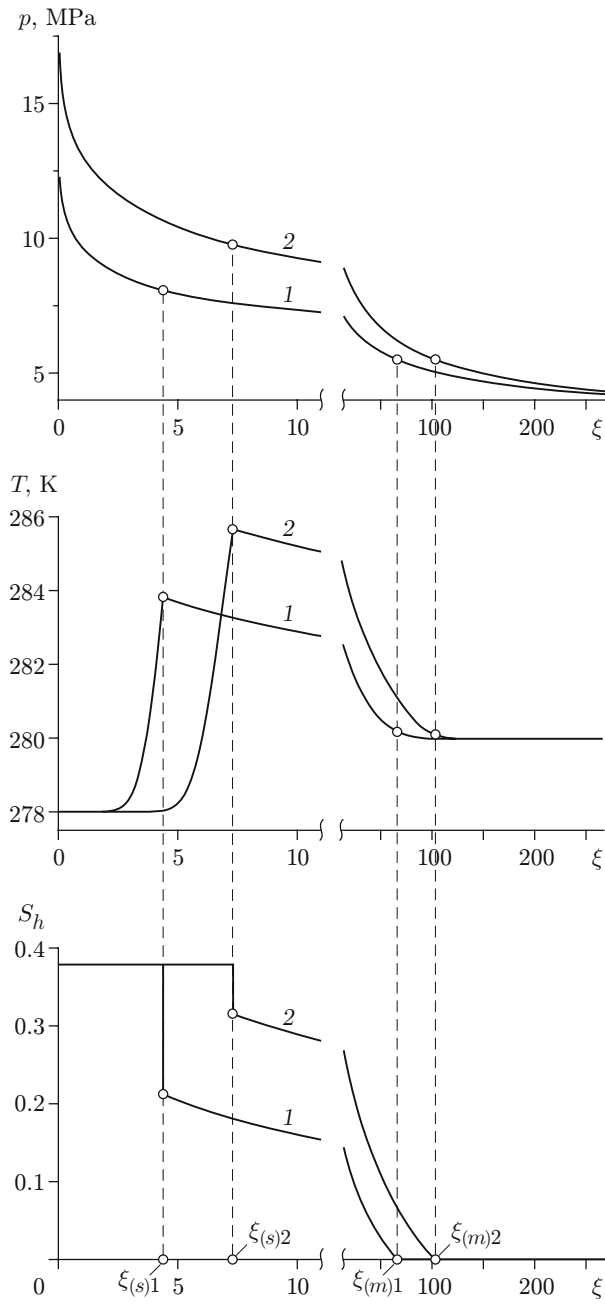
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Fig. 3

Fig. 4

Fig. 3. Distributions of temperature T and saturation by the hydrate S_h for $T_w = 276$ K, $S_{l0} = 0.2$, and different values of the mass flow rate of the gas (the remaining parameters are identical to those in Fig. 1): $Q_g = 0.035$ (1), 0.04 (2), and 0.045 kg/(m·sec) (3).

Fig. 4. Distributions of pressure p, temperature T, and saturation by the hydrate S_h for $S_{l0} = 0.3$ and different values of the mass flow rate of the gas: $Q_g = 0.1$ (1) and 0.2 kg/(m·sec) (2).

If condition (3.19) is satisfied, the volume zone of hydrate formation transforms to the frontal surface. Indeed, the system of equations for the first boundary (3.10) implies that

$$(T_{(s)} - T_w) \exp\Big(-\frac{\xi_{(s)}^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2} p_{(s)}^2 \Big) \Big/ \int_0^{\xi_{(s)}} \frac{1}{\xi} \exp\Big(-\frac{\xi^2}{4} - \frac{\mathrm{Pe}_{(1)}}{2p_0^2} p_{(1)}^2 \Big) d\xi - \frac{\Delta T \,(S_{h(1)} - S_{h(s)})}{2} \xi_{(s)}^2$$

$$= \frac{T_*}{2k_{(2)}p_{(s)}^2} \Big(-\frac{Q_g \mu_g R_g T_w}{\pi} \exp\Big(-\frac{\xi_{(s)}^2}{4\eta_{(1)}} \Big) + K(S_{h(1)} - S_{h(s)})\xi_{(s)}^2 \Big). \tag{3.20}$$

Substituting relation (3.19) into Eq. (3.20), we obtain

$$\frac{\Delta T}{2} S_{h(s)}\xi_{(s)} = -\frac{T_*}{2k_{(2)}p_{(s)}^2} KS_{h(s)}\xi_{(s)}.$$

The only nontrivial ($\xi_{(s)} \neq 0$) solution of this equation is the solution

$$S_{h(s)} = 0.$$

Then, from Eq. (3.14) with allowance for Eq. (3.3), we obtain

$$T_{(s)} = T_{(m)}, \qquad p_{(s)} = p_{(m)},$$

and Eq. (3.17) yields

$$\xi_{(s)} = \xi_{(m)}.$$

Thus, if condition (3.19) is satisfied, the extended zone degenerates into the frontal surface, which allow us to consider the solution with the frontal boundary of phase transitions obtained in Sec. 2 as the limit case of the problem with hydrate formation in the volume zone.

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