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SELF-SIMILAR PROBLEM OF DECOMPOSITION OF GAS HYDRATES IN A POROUS MEDIUM UPON DEPRESSION AND HEATING

R. I. Nigmatulin, V. Sh. Shagapov, and V. R. Syrtlanov

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We consider the specifics of decomposition of gas hydrates under thermal and depressive action on a porous medium completely filled with a solid hydrate in the initial condition. The existence of volumetric-expansion zones, in which the hydrate coexists in equilibrium with water and gas, is shown to be possible in high-permeable porous media. The self-similar problems of hydrate decomposition upon depression and heating are studied. Ii is shown that there are solutions according to which hydrate decomposition can occur both on the surface of phase transitions and in the volumetric region. We note that, in the first case, decomposition is possible without heat supply to a medium and even with heat removal.

At present, great theoretical and practical interest in studying gas hydrates in porous media has arisen due to the fact that many technological processes occurring in the gas, petroleum, and chemical industry are accompanied by the formation of gas hydrates; deposits of the hydrates of natural gases can occur in porous strata. Many theoretical and experimental investigations of gas hydrates are directed to the development of effective methods of preventing their formation in the extraction, transportation, and treatment of gases.

Some aspects of gas-hydrate decomposition in a porous medium completely filled with a hydrate in the initial state were studied in [1–4]. In addition, as shown in [5, 6], decomposition of hydrates that do not completely occupy a porous medium in the initial state is possible in the volumetric zone if a solid hydrate coexists with the decomposition products (gas and water).

In this paper, within the framework of self-similar solutions, we consider the specifics of gas-hydrate decomposition under thermal and depressive action on a porous medium completely filled with a solid hydrate in the initial state.

1. We consider filtration processes in a porous medium completely filled with a solid hydrate in the initial state. In describing decomposition processes, the following assumptions are usually adopted: the skeleton of a porous medium, a hydrate, and water are incompressible and immobile, the porosity m is constant, and the gas is calorically perfect:

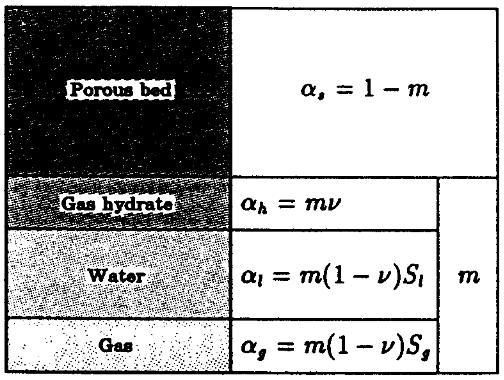
$$\rho_s^0, \rho_h^0, \rho_l^0, m = \text{const}, \quad \rho_g^0 = p/R_gT, \quad v_s = v_h = v_l = 0.$$

Here ρ_i^0 and v_i ($i = s$, h, l, g) are the densities and velocities of the phases, p and T are the pressure and the temperature, m is the porosity, and R_g is a gas constant; the subscripts s, h, l, and g refer to the porous-medium, hydrate, fluid, and gas parameters, respectively.

For the volumetric contents of the phases α_i (Fig. 1), we have

$$\alpha_s = 1 - m, \qquad \alpha_h = m\nu, \qquad \alpha_l = m(1-\nu)S_l, \qquad \alpha_g = m(1-\nu)S_g,$$
$$\alpha_s + \alpha_h + \alpha_l + \alpha_g = 1, \qquad S_g + S_l = 1,$$

Institute of Mechanics of Multiphase Systems, Siberian Division, Russian Academy of Sciences, Tyumen' 625000. Translated from Prikladnaya Mekhanika i Tekhnicheskaya Fizika, Vol. 39, No. 3, pp. 111–118, May–June, 1998. Original article submitted August 6, 1996.



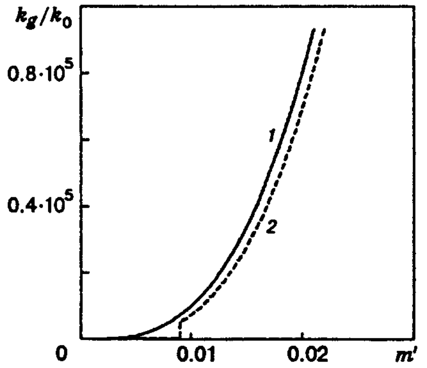


Fig. 1

Fig. 2

where ν is the saturation with water, i.e., the section of the porous volume occupied by a solid hydrate. The remaining section $1-\nu$ of the porous volume is occupied by a gas and water the amount of which is determined by the saturation with gas S_g and water S_l.

In a planar-dimensional approximation, the equations of conservation of masses, the Darcy law for decomposition products, and the heat-influx equation have the most general form in the volumetric-expansion zone:

$$\frac{\partial}{\partial t}[m(1-\nu)\rho_g^0 S_g] + \frac{\partial}{\partial x}[m(1-\nu)\rho_g^0 S_g v_g] = J_g, \quad \frac{\partial}{\partial t}[m(1-\nu)\rho_l^0 S_l] = J_l,$$

$$\frac{\partial}{\partial t}[m\nu\rho_h^0] = -J, \quad J_g + J_l = J, \quad J_g = gJ, \quad J_l = (1-g)J \tag{1.1}$$

[J_i ($i = l$, g) is the intensity of formation of the ith phase];

$$m(1-\nu)S_g v_g = -\frac{k_g}{\mu_g}\frac{\partial p}{\partial x} \tag{1.2}$$

[k_g and μ_g are the permeability and dynamic viscosity for the gas phase ($k_l = 0$)];

$$\rho c\frac{\partial T}{\partial t} + m(1-\nu)\rho_g^0 S_g c_g v_g \frac{\partial T}{\partial x} = m(1-\nu)S_g\left(\frac{\partial p}{\partial t} + v_g\frac{\partial p}{\partial x}\right) + \frac{\partial}{\partial x}\left(\lambda\frac{\partial T}{\partial x}\right) + lJ\frac{\partial \nu}{\partial t} \tag{1.3}$$

$$(\rho c = (1-m)\rho_s^0 c_s + m[(1-\nu)(\rho_g^0 S_g c_g + \rho_l^0 S_l c_l) + \nu\rho_h^0 c_h]).$$

Here c_i are the specific heat capacities, c_g is the heat capacity of the gas at constant pressure, l is the specific heat of hydrate decomposition, and g is the mass fraction of the gas in the hydrate.

A gas hydrate with a porous skeleton forms an absolutely solid body, and the pressure distribution in it can be arbitrary with one thermodynamic condition of hydrate stability [$p \geqslant p_s(T)$]. By an arbitrary pressure in a hydrate with a porous skeleton, we mean any distribution of stresses (with the first invariant governing the pressure) which satisfy the equations of statics, the boundary conditions, and the thermodynamic conditions of existence of a gas hydrate. In the three-phase zone, where α_h, α_l, and $\alpha_g > 0$, the condition of equilibrium phase transitions [$T = T_s(p)$] is assumed. Thus, the dependence of the phase-equilibrium temperature on the pressure is taken in the form

$$T_s(p) = T_{s0} + T_* \ln(p/p_{s0}), \tag{1.4}$$

where T_{s0} is the phase-transition temperature which corresponds to the pressure p_{s0} and T_* is an empirical parameter (usually, $T_* \ll T_{s0}$). According to the Clapeyron–Clausius equation, we have

$$\frac{dT_s}{dp} = \frac{T_s}{l}\left(\frac{1}{\rho_{gl}^0} - \frac{1}{\rho_h^0}\right), \quad \frac{1}{\rho_{gl}^0} = \frac{g}{\rho_{gs}^0(p)} + \frac{1-g}{\rho_l^0}.$$

Here the gas density on the line of gas-hydrate saturation is $\rho^0_{gs}(p) = \rho^0_g(p, T_s(p)) = p/R_g T_s(p)$. With allowance for (1.4), we obtain

$$\frac{T_s(p)}{l(p)}\left[g\left(\frac{1}{\rho^0_{gs}(p)} - \frac{1}{\rho^0_l}\right) + \left(\frac{1}{\rho^0_l} - \frac{1}{\rho^0_h}\right)\right] = \frac{T_*}{p}.$$

For the problems considered, the variability of l turns out to be insignificant. For example, within the pressure range $p = 5$–15 MPa, for the methane hydrate we have $l = (5 \cdot 10^5 \pm 2 \cdot 10^2)$ J/kg.

The coefficient of gas permeability depends on the volumetric concentration of the gas (or the "effective" porosity). We specify this dependence on the basis of the Kozeny formula (the solid curve in Fig. 2)

$$k_g = k_0 \frac{m'^3}{(1 - m')^2} \simeq k_{g0} S_g^3 (1 - \nu)^3 \qquad (m' = \alpha_g,\ k_{g0} = k_0 m^3), \tag{1.5}$$

where m' is the "effective" porosity for the gas. Specifying the permeability coefficient in this form assumes that the characteristic sizes of "effective" pores are the same as those for the solid skeleton. Basically, this dependence in the zone of formation of the "effective" porosity, where it is small and can be shown as bubbles or others uncombined or weakly combined microvolumes, should be refined by introducing the ultimate "effective" porosity m'_* below which $(0 \leqslant m' \leqslant m'_*)$ the permeability is equal to zero (the dashed curve in Fig. 2).

Taking into account that, in the initial state, the porous medium is completely filled with a hydrate, for S_g and S_l, according to [4] we have

$$S_l = \frac{(1 - g)\rho^0_h}{\rho^0_l}, \qquad S_g = \frac{\rho^0_l - (1 - g)\rho^0_h}{\rho^0_l}. \tag{1.6}$$

In the decomposition of hydrates, three zones can be formed, each containing only the solid hydrate, or the hydrate and the decomposition products, or the decomposition products. At the boundaries of these zones, the relations that follow from the law of conservation of mass and the heat balance should be fulfilled:

$$[m((1 - \nu)\rho^0_g S_g (v_g - \dot{x}_{(s)}) - \nu g \rho^0_h \dot{x}_{(s)})] = 0; \tag{1.7}$$

$$\left[\lambda \frac{\partial T}{\partial x}\right] = -[m\nu \rho^0_h l \dot{x}_{(s)}] \qquad \left([\psi] = \psi_+ - \psi_-,\ \dot{x}_{(s)} = \frac{dx_{(s)}}{dt}\right). \tag{1.8}$$

Here $[\psi]$ is the jump of the parameter ψ at the boundary $x_{(s)}$ between the zones. The temperature and the pressure at these boundaries are assumed to be continuous.

2. Three cases can be distinguished at the boundary under the simultaneous thermal and depressive action of a porous medium through the boundary ($x = 0$), depending on the values of temperature T_e and pressure p_e. In the first case, the temperature and the pressure at the boundary are higher than T_0 and p_{s0} ($T_e > T_0$ and $p_e > p_{s0}$), where p_{s0} is the equilibrium pressure at temperature T_0. Here, for the self-similar problem of an abrupt change of the temperature and pressure, one can construct only the solution with the surface of the phase transition. For two other cases ($T_e > T_0$, $p_e < p_{s0}$ and $T_e < T_0$, $p_e < p_{s0}$), it is possible to construct both the solution with the phase-transition surface and, under certain conditions for permeability of the porous medium, the solution that contains the volumetric-expansion zone.

Using a self-similar substitution $\xi = x/\sqrt{a^{(T)}t}$ $[a^{(T)} = \lambda/\rho c]$, we reduce system (1.1)–(1.8) to the system of ordinary differential equations:

$$-\frac{\xi}{2}\frac{d}{d\xi}[(\mathcal{R}_g - \mathcal{R}_h)(1 - \nu)] = \frac{d}{d\xi}\left(K\mathcal{R}_g \frac{dP}{d\xi}(1 - \nu)^3\right),$$

$$-\frac{\xi}{2}\frac{d\Theta}{d\xi} + \eta K (1 - \nu)^3 \frac{dP}{d\xi}\frac{d\Theta}{d\xi} = \frac{d^2\Theta}{d\xi^2} + \chi(1 - \nu)\left[-\frac{\xi}{2}\frac{dP}{d\xi} + K(1 - \nu)^2\left(\frac{dP}{d\xi}\right)^2\right] - \Theta_{**}\frac{\xi}{2}\frac{d\nu}{d\xi},$$

$$P = \frac{p}{p_0}, \quad \Theta = \frac{T}{T_0}, \quad \mathcal{R}_g = \frac{\rho^0_g}{\rho^0_{g0}}, \quad K = \frac{k_{g0} p_0 S_g}{m\mu_g a^{(T)}}, \quad \rho^0_{g0} = \frac{p_{s0}}{RT_0}, \tag{2.1}$$

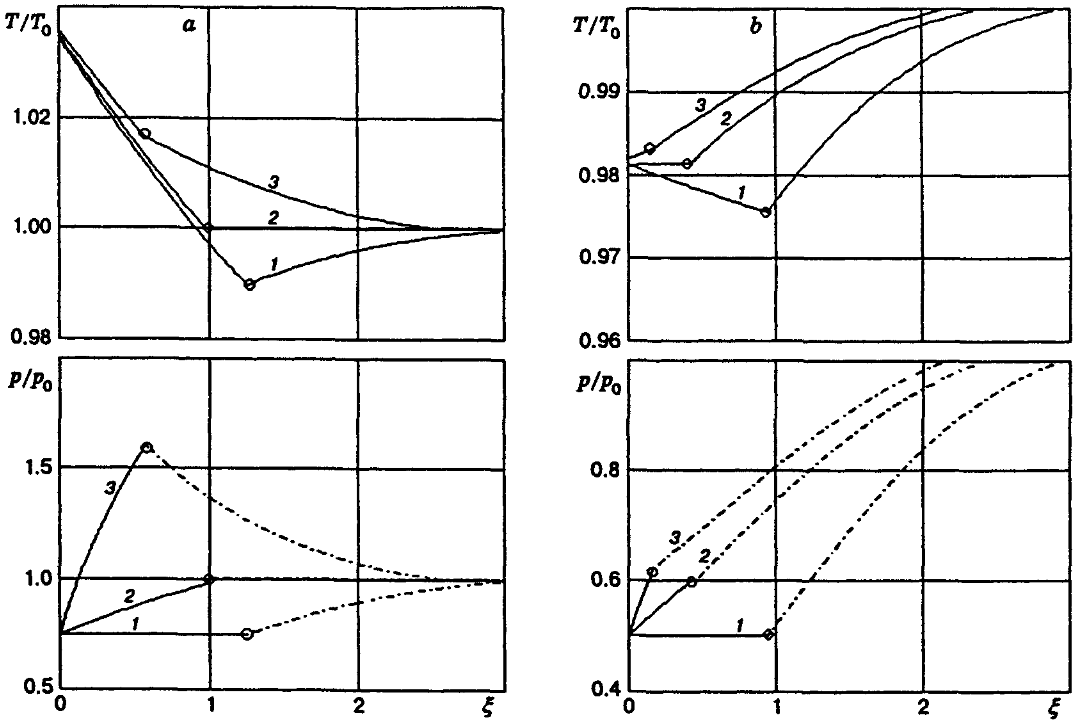


Fig. 3

$$\mathcal{R}_g = \frac{P}{\Theta}, \quad \eta = mS_g\frac{\rho_{g0}^0 c_g}{\rho c}, \quad \chi = \eta\frac{R}{c_g}, \quad \mathcal{R}_h = \frac{g\rho_h^0}{S_g\rho_{g0}^0}, \quad \Theta_{**} = \frac{m\rho_h^0 l}{\rho c T_0}.$$

The equations are derived from (2.1) for $\nu = 1$ in the region where the porous medium is completely filled with a solid hydrate and for $\nu = 0$ in the region where the porous medium is saturated by the decomposition products of the hydrate. Here on the surface of the water-saturated jump, according to (1.6), the boundary conditions take, in self-similar coordinates, the form

$$\left[\frac{d\Theta}{d\xi}\right] = \left[\Theta_{**}\nu\frac{\xi_{(s)}}{2}\right], \quad \left[K(1-\nu)^3\left(\frac{dP}{d\xi}\right)\right] = \left[\nu\left(\frac{\mathcal{R}_h}{\mathcal{R}_g} - 1\right)\frac{\xi_{(s)}}{2}\right],$$

whereas $P = P_e$, $\Theta = \Theta_e$ ($\xi = 0$) at the boundary of the porous medium and $\Theta = 1$ ($\xi = \infty$) at infinity. The system was integrated for the following values of the parameters of the hydrate–porous medium system: $m = 0.1$, $T_0 = 283$ K, $\rho_{s0} = 5.08$ MPa, $T_* = 10$ K, $p_* = 2.6 \cdot 10^{-6}$ Pa, $\rho_s^0 = 2 \cdot 10^3$ kg/m³, $\rho_h^0 = 0.9 \cdot 10^3$ kg/m³, $\rho_l^0 = 10^3$ kg/m³, $\mu_g = 1.8 \cdot 10^{-5}$ Pa· sec, $\lambda_s = 2$ kg·m/(sec³·K), $\lambda_h = 2.11$ kg·m/(sec³·K), $\lambda_l = 0.58$ kg·m/(sec³·K), $\lambda_g = 3 \cdot 10^{-2}$ kg·m/(sec³·K), $c_s = 1000$ J/(kg·K), $c_h = 2500$ J/(kg·K), $c_l = 4200$ J/(kg ·K), $l = 5 \cdot 10^5$ J/kg.

Figure 3a shows a solution that corresponds to the simultaneously occurring heating and depression ($T_e > T_0$, $p_e < p_{s0}$); curves 1–3 refer to the permeability of the skeleton $k_{g0} = 10^{-13}$, 10^{-16}, and 10^{-17} m². Two types of solutions are possible, depending on the magnitude of k_{g0}. The first case (curve 3) occurs for sufficiently low permeability, and here the temperature on the phase-transition surface is higher than the initial temperature of the hydrate (it is worth noting that in the case of heating with a simultaneous increase in the pressure at the boundary of the porous medium, the solution will be qualitatively the same). The second case occurs for sufficiently high permeability (curve 1) and differs from the first in that the temperature at the phase-transition surface is lower than the initial temperature of the system. In this case, hydrate decomposition occurs also owing to heat influx from the system being in the zone in front of the phase-transition surface in heated state. The two types of solutions are separated by an intermediate solution (curve 2) according to which the temperature in the solid-hydrate zone is constant. The dot-and-dashed curves in this and subsequent figures correspond to the equilibrium pressure $p_s(T)$ in the zone filled with the solid hydrate, and circles to the position of the phase-transition front.

Of interest is the situation shown in Fig. 3b, where the temperature at the boundary is lower than the initial temperature T_0 ($T_e < T_0$ and $p_e < p_{s0}$). In this case, two types of solutions are possible as well. Curve 1 with a temperature "pit" near the boundary of the porous medium corresponds to a first-type solution. Such solutions are realized for sufficiently high permeability of a porous medium and are characterized by that the heat is supplied from the boundary to the phase-transition surface, although the temperature at the boundary of the porous medium is lower than the initial temperature. This is caused by the fact that in decomposing the hydrate, the temperature on the surface of the phase transitions decreases even more owing to depression ($p_e < p_{s0}$) and becomes lower than that of the boundary of the porous medium. The decomposition in this case is caused by heat influx both from the zone of the initial solid hydrate and from the boundary. For second-type solutions (curve 3), which are obtained for low permeability, the depression-induced "hydrate superheating" is sufficient not only for hydrate decomposition, but also for heat efflux from the porous medium to its boundary (by "superheating," we mean a positive difference between the initial temperature and the temperature at the hydrate-decomposition front). For the intermediate solution (curve 2), the heat flux at the boundary is equal to zero. In this case, decomposition occurs owing to the heat released by the "superheated" hydrate.

3. For the system of equations considered, one can construct a solution that contains the third (intermediate) three-phase volumetric region, where the hydrate and the decomposition products coexist simultaneously. In the general case, it is necessary to introduce two phase-transition surfaces: the surface $\xi^{(p)}_{(s)}$ between the three-phase zone, where the solid hydrate and a gas–liquid mixture are present, and the zone of a pure hydrate and the surface $\xi^{(T)}_{(s)}$ between the zone where there are only the decomposition products and the three-phase zone.

The system of equations in this case coincides with (2.1), and the phase-equilibrium condition for a hydrate (1.4) being added in the region $\xi^{(T)}_{(s)} < \xi < \xi^{(p)}_{(s)}$. We write the boundary conditions in the form

$$K(1-\nu^-)^2\left(\frac{dP}{d\xi}\right)^- = \left(\frac{\mathcal{R}^0_{h*}}{\mathcal{R}^{0(p)}_{g(s)}} - 1\right)\frac{\xi^{(p)}_{(s)}}{2}, \quad \left(\frac{d\Theta}{d\xi}\right)^+ - \left(\frac{d\Theta}{d\xi}\right)^- = \Theta_{**}(1-\nu^-)\frac{\xi^{(p)}_{(s)}}{2} \tag{3.1}$$

for $\xi = \xi^{(p)}_{(s)}$ and

$$K\left(\frac{dP}{d\xi}\right)^- - K(1-\nu^+)^2\left(\frac{dP}{d\xi}\right)^+ = \nu^+\left(\frac{\mathcal{R}^0_{h*}}{\mathcal{R}^{0(T)}_{g(s)}} - 1\right)\frac{\xi^{(T)}_{(s)}}{2}, \quad \left(\frac{d\Theta}{d\xi}\right)^+ - \left(\frac{d\Theta}{d\xi}\right)^- = \Theta_{**}\nu^+\frac{\xi^{(T)}_{(s)}}{2} \tag{3.2}$$

for $\xi = \xi^{(T)}_{(s)}$.

If the maximum value of the coefficient of gas permeability k_g, which is reached for $\nu = 0$, is rather large and it is also subject to the condition $a^{(p)}/a^{(T)} > 2$, system (2.1) admits a set of solutions that contains the intermediate three-phase region for given temperature and pressure values at the boundary of a porous medium. This set of solutions "extends" from the solution with one phase-transition surface $\left[\xi_{(s)} = \xi^{(T)}_{(s)} = \xi^{(p)}_{(s)}\right]$, when the saturation with water at the boundary varies from the initial value $\nu^+ = 1$ to $\nu^- = 0$, to the limiting solution, when the saturation with water varies from $\nu^+ = 1$ to $\nu^- = \nu_m$ ($\nu_m > 0$) at the frontal boundary [$\xi = \xi^{(p)}_{(s)}$]. In other words, one can construct a solution for any value of saturation with water ν^- from the side of the three-phase zone on the surface between this zone and the pure-hydrate zone ($\nu = 1$), which is subject to the condition $0 \leqslant \nu^- \leqslant \nu_m$. We note that the limiting saturation with water ν_m depends on the maximum value of the permeability coefficient $k_g(\nu)$. For $\nu^- > \nu_m$, there is no solution entering into the indicated set, and this, in turn, means, that, in the case $\nu^- > \nu_m$, in the three-phase region the pressure field, which, according to (1.4), is uniquely determined by the temperature field, is not capable of transporting the products of hydrate decomposition (the gas in this case) through a porous medium. We note that the principle of selection of a unique solution is generally unknown and calls for further analysis. The set of solutions can

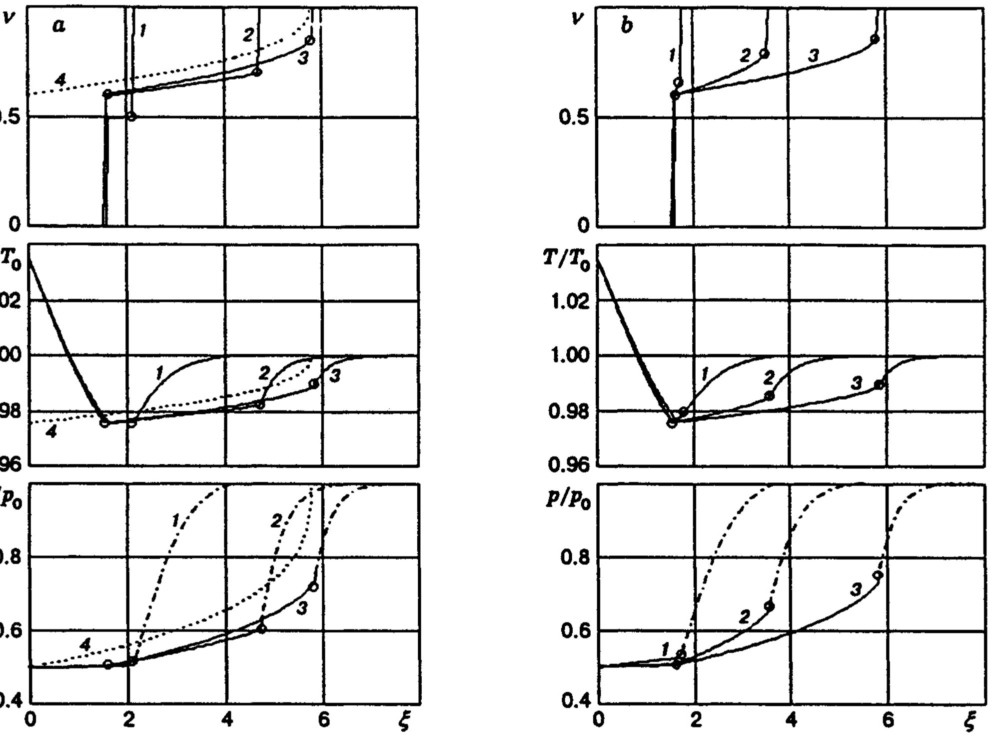


Fig. 4

be narrowed if, for example, one assumes that in the "effective"-porosity formation zone (when the saturation with water is close to unity), the gas is a system of uncombined or weakly combined microvolumes. Here gas filtration begins when the saturation with water becomes lower than some critical value $\nu = \nu^*$. The corresponding value of the "effective" porosity is larger than m'_* (the dashed curve in Fig. 2). If this critical saturation with water ν^* is smaller than the limiting value ν_m, the range 0–ν^* is the domain of values for ν^-.

Figure 4a shows solutions for $k_{g0} = 10^{-13}$ m^2 that correspond to various values of the saturation with water ν^-. The limiting value of the saturation with water is $\nu_m = 0.96$. Curves 1–3 correspond to various water-saturated jumps at the boundary of partial decomposition, and curve 4 to the solution without account for the thermal conduction obtained in [4].

Another possibility of the choice of an additional condition consists in analysis of the boundary conditions (3.1) and (3.2); with allowance for the solution of Eq. (2.1) in the solid-hydrate zone, neglecting $\mathcal{K}_g^0$ in comparison with $\mathcal{K}_{h*}^0$, one obtains

$$1 - \Theta^{(p)}_{(s)} = \Theta_{**}(1 - \nu^-)(1 + a^{(p)}/a^{(T)})/\varphi(\xi^{(p)}_{(s)}). \tag{3.3}$$

With a fixed self-similar coordinate $\xi^{(p)}_{(s)}$, relation (3.3) relates the temperature at the boundary of partial phase transitions to the saturation with water at this boundary. It is noteworthy that, for some value of $\nu^- = \nu_m$, the quantity $1 - \Theta^{(p)}_{(s)}$ has a minimum, so that $a^{(p)}/a^{(T)} = 2$. Clearly, the left branch of the dependence of $1 - \Theta^{(p)}_{(s)}$ on $1 - \nu^-$ has no physical meaning, because here to the larger temperature drop between the initial temperature of the system and the temperature on the surface of a partial phase transition corresponds the smaller saturation-with-water drop (i.e., the more intense heat flux ensures a weaker phase transition). Thus, there is a maximum value of the saturation with water ν_m, for which solutions with volumetric decomposition of the hydrate are still possible. In other words, we always should have $a^{(p)}/a^{(T)} > 2$ ($\nu < \nu_m$) in the three-phase zone. For a low-permeability porous medium, when $a^{(p)}/a^{(T)} < 2$, it is impossible to construct a solution with the volume decomposition zone for all ν. In this case, there is a unique solution, according to which the decomposition will occur on the phase-transition surface.

Figure 4b shows a parameter distribution for limiting solutions (when $\nu^- = \nu_m$) for $k_{g0} = 10^{-14}$, $4 \cdot 10^{-14}$, and 10^{-13} m^2 (curves 1–3). It is seen that as the permeability deteriorates, the hydrate-decomposition zone narrows, becoming, in the limit, the surface of phase transitions.

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