Journal of Engineering Physics and Thermophysics, Vol. 74, No. 5, 2001

REGIMES OF DISSOCIATION OF GAS HYDRATES COEXISTING WITH A GAS IN NATURAL STRATA

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UDC 532.546:536.421

A mathematical model of decomposition of gas hydrates that coexist with a gas in natural strata is proposed; the model takes into account the mobility of the liquid phase. Conditions at the unknown boundary of dissociation are derived. In the self-similar approximation, the solution is represented in the form of probability integrals. The obtained system of transcendental equations at the moving boundary has been investigated numerically in a wide range of parameters. It is shown that different regimes of dissociation in collectors with a positive initial temperature exist; these regimes correspond to the decomposition of a hydrate into gas and water and gas and ice and have both a sharp phase-transition front and are accompanied by the formation of an extended region of dissociation. On the plane of the main parameters of the process, the critical diagram is constructed and the existence domains of the solution of each form are singled out.

Interest in gas hydrates, as in potential sources of natural gas, has grown in recent years. The supply of hydrates found in different regions of the world turned out to be so considerable that the development of scientifically intensive technologies of extraction of a gas from the natural deposits of gas hydrates is one of the main problems in this stage. Permeable strata that can contain natural gas in the free state, water, petroleum, etc. in addition to gas hydrates are one of the most widespread kinds of deposits of gas hydrates.

The process of extraction of a gas from a hydrate-containing stratum assumes the decomposition of the hydrate in the stratum and is accompanied by the motion of the gas, water, petroleum, or other mobile components contained in the collector and by phase transitions as well. In the general case we can have different regions separated by interphase boundaries at which phase transitions of various nature occur [1–5].

Equations of multiphase nonisothermal filtration that are supplemented with conditions at the unknown moving boundary underlie the mathematical description of such processes. The formulated problems are rather complex; the existence and uniqueness theorems are not proved in them, and the employment of numerical methods is currently retarded by the absence of a clear understanding of the qualitative characteristics of the thermodynamic behavior of the hydrate-containing system. In this connection, exact solutions are of primary importance in the present stage of investigation of the process of dissociation of hydrates in strata; these solutions make it possible to analyze in detail the basic properties of the physical system and to determine possible structures of mathematical solution of the problem. However, even in the simplest cases one is unable to find a purely analytical solution of the problem since the analytical solutions obtained in each existence domain of the phases lead to a system of transcendental equations at a moving boundary that can be investigated just by numerical methods.

In the present work, we formulate a mathematical model of dissociation of gas nitrates coexisting with a gas in permeable strata which takes into account the mobility of the liquid phase. The one-dimensional problem is investigated in a self-similar formulation. The calculations performed in a wide parameter range

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indicate the existence of four different regimes of dissociation. A critical diagram is constructed on the plane of the main parameters and the existence domain of the solution of each form for each kind of regime are singled out.

1. We will assume that the hydrate-containing stratum is a porous medium saturated with a gas hydrate and a gas. Let us assume that the operation of a gas well reduces the pressure in the stratum, leading to the dissociation of the hydrate and the formation of a region saturated with water and gas. The assumption is made that in the heterogeneous mixture gas–water the latter acts as an incompressible fluid. The system of basic equations represents the laws of conservation of mass and energy, Darcy's law, the equation of state for a gas, and thermodynamic relations; the system has the following form:

- in the region gas–hydrate

$$m\frac{\partial}{\partial t}(1-\nu)\,\rho_g+\mathrm{div}\,\rho_g\mathbf{v}_g=0\,,\quad \mathbf{v}_g=-\frac{k}{\mu_g}f_g(\nu)\,\mathrm{grad}\,P\,,\ P=\rho_gRT\,,$$

$$(\rho C)_1\frac{\partial T}{\partial t}+\mathrm{div}\,(\mathbf{v}_g P)+C_V\rho_g\mathbf{v}_g\,\mathrm{grad}\,T=\mathrm{div}\,(\lambda_1\,\mathrm{grad}\,T)\,,\tag{1}$$

$$\lambda_1=m\nu\lambda_h+m(1-\nu)\,\lambda_g+(1-m)\,\lambda_s\,,\ (\rho C)_1=m\nu\rho_hC_h+m(1-\nu)\,\rho_gC_g+(1-m)\,\rho_sC_s\,;$$

- in the region gas–water

$$m\frac{\partial}{\partial t}(1-S)\,\rho_g+\mathrm{div}\,\rho_g\mathbf{v}_g=0\,,\ m\frac{\partial}{\partial t}S+\mathrm{div}\,\mathbf{v}_w=0\,,\ \mathbf{v}_j=-\frac{k}{\mu_j}f_j(S)\,\mathrm{grad}\,P\,,\ \ j=\mathrm{w,\,g}\,,$$

$$(\rho C)_2\frac{\partial T}{\partial t}+\mathrm{div}\,[P(v_g+v_w)]+(\rho_wC_w\mathbf{v}_w+\rho_gC_g\mathbf{v}_g)\,\mathrm{grad}\,T=\mathrm{div}\,(\lambda_2\,\mathrm{grad}\,T)\,,\tag{2}$$

Conditions on the front of decomposition of the hydrate are formulated as the conditions of a thermodynamically equilibrium jump of the functions of hydrate and water saturation. The conditions of thermodynamic equilibrium on the dissociation surface of the hydrate have the form

$$P=\rho_gRT\,,\quad \lambda_2=mS\lambda_w+m(1-S)\,\lambda_g+(1-m)\,\lambda_s\,,\ (\rho C)_2=mS\rho_wC_w+m(1-S)\,\rho_gC_g+(1-m)\,\rho_sC_s\,.$$

$$T_+=T_-=T_*\,,\quad P_+=P_-=P_*\,,\quad \ln P_*=A-\frac{B}{T_*}\,,\quad A=49.32\,,\quad B=9459\,.\tag{3}$$

The last relation that represents an analytical relationship between the pressure and the dissociation temperature of the gas hydrate is obtained as a result of interpolation of experimental data [6].

The second group of boundary conditions on the dissociation surface represents the laws of conservation of the masses of the gas and the water and also the law of conservation of energy

$$m\left(\nu_+\frac{\rho_{0g}}{\rho_g}+S_--\nu_+\right)V_n=\frac{kf_g(\nu_+)}{\mu_g}(\mathrm{grad}\,P)_{n+}-\frac{kf_g(S_-)}{\mu_g}(\mathrm{grad}\,P)_{n-}\,,\tag{4}$$

$$m\left(\nu_+\frac{\rho_{0w}}{\rho_w}-S_-\right)V_n=\frac{kf_w(S_-)}{\mu_w}(\mathrm{grad}\,P)_{n-}\,,\ m\nu_+q\rho_hV_n=(\lambda\,\mathrm{grad}\,T)_{n+}-(\lambda\,\mathrm{grad}\,T)_{n-}\,.$$

The system of the laws of conservation (4) at the unknown moving boundary together with the conditions of thermodynamic equilibrium (3) comprises the complete system of boundary conditions on the dissociation surface.

2. We consider the problem of decomposition of a hydrate in a semiinfinite stratum. Let the half-space $x > 0$, at the initial instant of time, be occupied by a stratum filled with a heterogeneous mixture of a hydrate and a gas with the temperature T_0, pressure P_0, and value of the hydrate saturation $\nu = \nu_0$. We assume that on a stationary wall $x = 0$ that corresponds to the producing well (or system of wells) the pressure decreased to a certain rather small value P^0 that corresponds to the thermodynamic conditions of existence of the gas in a free state. Then the hydrate-dissociation front $x = X(t)$ that separates the regions saturated with the mixtures gas–hydrate and gas–water, respectively, propagates to the right of the surface $x = 0$.

We consider dissociation regimes that correspond to the technology of decomposition of the hydrate by the method of reducing the stratum pressure. In this case, the change in the stratum temperature is attributed to the absorption of heat as a consequence of the decomposition of the hydrate. We establish the upper limit of variation of the temperature for a unit volume of the hydrate-containing stratum. Disregarding the external inflow of heat to this volume gives the maximum value for the decrease in the stratum temperature. The law of conservation of energy yields the relation between variations of temperature and those of hydrate saturation:

$$(1 - m)\,\rho_s C_s \delta T \approx m \rho_h q \delta\nu\ .$$

By substituting the characteristic value of the parameters we obtain

$$0.8 \cdot 2 \cdot 10^3 \cdot 10^3 \delta T \approx 0.2 \cdot 0.9 \cdot 10^3 \cdot 5 \cdot 10^5 \cdot 0.5\ .$$

It follows that the characteristic value for the maximum change in the temperature in the case of dissociation of a gas hydrate in the stratum is $\delta T \le 30$ K.

It should be noted that the actual change in the temperature is smaller because of the presence of the influx of heat to the singled-out volume. The above upper limits make it possible to infer that under the depression action on a hydrate-containing stratum the variation of temperature is much smaller than the absolute value; therefore, the procedure of linearization relative to the temperature function is always true.

We consider the ratio of convective transfer to conductive transfer in the energy equation that is determined by the dimensionless parameter $\dfrac{\rho_w C_w}{\mu_w \lambda_1} k\delta P$. The characteristic values of the pressure and the permeability coefficient can be changed considerably, whereas the changes in the remaining parameters are small; therefore, the condition of smallness of the convective transfer of heat can be written in the form

$$\frac{\rho_w C_w}{\mu_w \lambda_1} k\delta P \approx \frac{10^3 \cdot 4.4 \cdot 10^3}{2 \cdot 10^{-3} \cdot 1.8} k\delta P \approx 10^9\, k\delta P << 1\ .$$

Finally, we obtain the condition of smallness of the convection transfer of energy in the region gas–water in the form $k\delta P << 10^{-9}$ N.

Analogous considerations performed for the region gas–hydrate lead to the relation

$$\frac{\rho_g C_P}{\mu_g \lambda_2} k\delta P \approx \frac{2.6 \cdot 2 \cdot 10^3}{10^{-5} \cdot 1.8} k\delta P \approx 2.9 \cdot 10^8\, k\delta P << 1\ .$$

The condition obtained in the region gas–hydrate is weaker; therefore, it will suffice to set a limit to the smallness of the convective flow in the region gas–water; then the analog condition in the region gas–hydrate will be fulfilled automatically. Assuming that the pressure changes are small as compared to the absolute values and the temperature changes, as has been shown above, are in the order of tens of degrees, upon disregarding the small terms in systems (1) and (2) we obtain a system of linear equations for disturbances in the regions gas–water and hydrate–gas respectively:

$$\frac{\partial S'}{\partial t} = \kappa_{\rm w} \Delta P' , \quad \frac{\partial P'}{\partial t} = \kappa_j \Delta P' , \quad \frac{\partial T}{\partial t} = a_j \Delta P , \quad j = 1, 2 ;$$

$$\kappa_{\rm w} = \frac{kf(S^0)}{m\mu_{\rm w}} , \quad \kappa_1 = \frac{kP_0}{m\mu_{\rm g}} , \quad \kappa_2 = \left[\frac{S^0}{\mu_{\rm w}} + \frac{1 - S^0}{\mu_{\rm g}}\right] \frac{kP^0}{m\,(1 - S^0)} ,$$

$$a_1 = \frac{m\nu_0 \lambda_{\rm h} + m\,(1 - \nu_0)\,\lambda_{\rm g} + (1 - m)\,\lambda_{\rm s}}{m\nu_0\,\rho_{\rm h} C_{\rm h} + m\,(1 - \nu_0)\,\rho_{\rm g} C_{\rm g} + (1 - m)\,\rho_{\rm s} C_{\rm s}} ,$$

$$a_2 = \frac{mS^0 \lambda_{\rm w} + m\,(1 - S^0)\,\lambda_{\rm g} + (1 - m)\,\lambda_{\rm s}}{mS^0\,\rho_{\rm w} C_{\rm w} + m\,(1 - S^0)\,\rho_{\rm g} C_{\rm g} + (1 - m)\,\rho_{\rm s} C_{\rm s}}$$

(S^0 is the undisturbed water saturation in the region gas–water which depends on the initial hydrate saturation and is calculated from the formula $S^0 = \nu_0 \rho_{\rm h} / \rho_{\rm w}$).

The initial and boundary conditions have the form

$$t = 0 : \ \ X(0) = 0 , \quad x > 0 : \ \ T = T_0 , \ \ P = P_0 ; \quad x = 0 : \ \ P = P^0\ (P^0 < P_0) , \quad T = T^0 .$$

We consider the case where the hydrate saturation of the stratum and the initial and boundary values of the temperature and the pressure are constant. Then the problem has a self-similar solution of the form

$$X(t) < x < \infty : \ \ T(\zeta) = (T_* - T_0)\,\frac{\mathrm{erfc}\,(\zeta)}{\mathrm{erfc}\,(\gamma)} + T_0 , \quad P(\zeta) = (P_* - P_0)\,\frac{\mathrm{erfc}\,(\zeta)}{\mathrm{erfc}\,(\gamma)} + P_0 ;$$

$$0 < x < X(t) : \ \ T(\zeta) = (T_* - T^0)\,\frac{\mathrm{erf}\,(\zeta)}{\mathrm{erf}\,(\gamma)} + T^0 , \quad P(\zeta) = (P_* - P^0)\,\frac{\mathrm{erf}\,(\zeta)}{\mathrm{erf}\,(\gamma)} + P^0 .$$

By substituting the expressions for the pressure and the temperature into the conditions at the moving boundary (3)–(4) we obtain the system of transcendental equation for γ, Θ_*, Π_*, and S_-

$$\sqrt{\frac{\pi a_1}{\kappa_1}} \left(\nu_0 \left(\frac{\rho_{0\rm g}}{\rho_{\rm g}} - 1\right) + S_-\right) \gamma + (1 - \nu_0)\,[\Pi_* - 1]\,\frac{\exp\,(-\gamma^2 a_1/\kappa_1)}{\mathrm{erfc}\,(\gamma \sqrt{a_1/\kappa_1})} -$$

$$- (1 - S_-) \sqrt{\frac{\kappa_1}{\kappa_2}} \left(\Pi_* - \frac{P^0}{P_0}\right) \frac{\exp\,(-\gamma^2 a_1/\kappa_2)}{\mathrm{erf}\,(\gamma \sqrt{a_1/\kappa_2})} = 0 , \tag{5}$$

$$\sqrt{\pi} \left(\nu_0 \frac{\rho_{0\rm w}}{\rho_{\rm w}} - S_-\right) \gamma - \frac{\kappa_{\rm w}}{\sqrt{a_1 \kappa_2}}\, S_- \left(\Pi_* - \frac{P^0}{P_0}\right) \frac{\exp\,(-\gamma^2 a_1/\kappa_2)}{\mathrm{erf}\,(\gamma \sqrt{a_1/\kappa_2})} = 0 ,$$

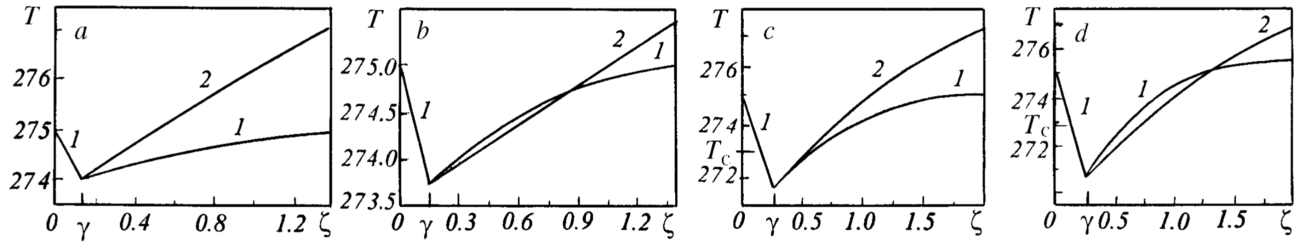

Fig. 1. Distribution of the stratum temperature (1) and the dissociation temperature of the hydrate (2): a) consistent case corresponding to the decomposition of the hydrate into the gas and the water ($P^0 = 2.5 \cdot 10^6$ Pa, $k = 10^{-17}$ m^2); b) superheating of the hydrate corresponding to the formation of an extended dissociation region ($P^0 = 2.5 \cdot 10^6$ Pa, $k = 5 \cdot 10^{-17}$ m^2); c) subcooling of the water behind the dissociation front corresponding to the formation of an ice "lock" behind the front ($P^0 = 1.3 \cdot 10^6$ Pa, $k = 10^{-17}$ m^2); d) superheating of the hydrate in the region ahead of the front and subcooling of the water behind the dissociation front corresponding to the formation of an extended region of dissociation of the hydrate and the appearance of ice ($P^0 = 1.5 \cdot 10^6$ Pa, $k = 2 \cdot 10^{-17}$ m^2). T, K.

$$\frac{\sqrt{\pi a_1 \kappa_1}\, m \nu_0 q \rho_h}{\lambda_1 T_0} \gamma + (\Theta_* - 1) \frac{\exp(-\gamma^2 \kappa_1 / a_1)}{\operatorname{erfc}(\gamma \sqrt{\kappa_1 / a_1})} + \frac{\lambda_2}{\lambda_1} \sqrt{\frac{a_1}{a_2}} \left(\Theta_* - \frac{T^0}{T_0} \right) \frac{\exp(-\gamma^2 \kappa_1 / a_2)}{\operatorname{erf}(\gamma \sqrt{\kappa_1 / a_2})} = 0 ,$$

$$\ln(\Pi_* P_0) = A - \frac{B}{T_0 \Theta_*} .$$

The condition of thermodynamic consistency of the solution implies that the temperature of the water in the region behind the hydrate-dissociation front must be higher than the crystallization temperature of the water; otherwise, for the found negative temperature the mathematical model must take into account the formation of ice in dissociation. Another thermodynamic condition that reflects the condition of existence of a hydrate in the region ahead of the decomposition front assumes that the local temperature of the hydrate must be lower than the local dissociation temperature which is calculated from the pressure distribution found in the process of solution. If this condition is violated, then in order to eliminate thermodynamic inconsistency we must introduce an extended region of dissociation of the hydrate.

3. The system of transcendental equations (5) was solved numerically. From the presented initial and bounding values of the pressure, temperature, and hydrate-saturation functions we determined the velocity of the moving boundary of dissociation and the values of the temperature and pressure on the front. The calculations were performed for the regimes of decomposition of the hydrate that are attributed to the pressure decrease in the stratum without taking into account the temperature action on the stratum. The influx of heat required for dissociation was carried out from both the region ahead of the front and the region behind the front. Taking account of the latter represents taking account of the influx of heat from the surrounding rocks. In the absence of thermal action on the stratum the pressure distribution is monotonic in character. The numerical experiments performed in a wide parameter range revealed four fundamentally different regimes of decomposition of gas hydrates in the stratum that originally coexist with a gas. Figure 1a gives examples of calculations indicating the existence of a consistent solution for the following values of the parameters [7] and the initial and boundary conditions:

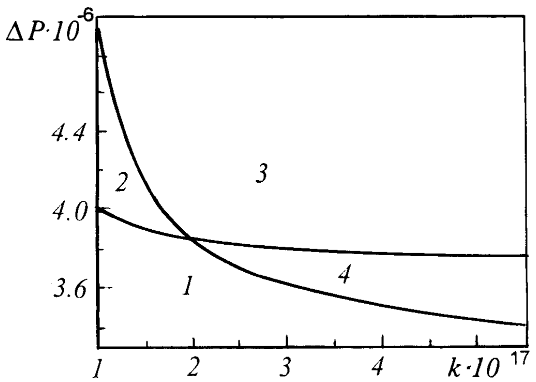

Fig. 2. Critical curves dividing the plane of parameters (k, P^0) into four existence domains of different dissociation regimes: 1) decomposition into the gas and the water; 2) decomposition with the formation of ice; 3) formation of ice and of an extended dissociation region; 4) formation of an extended dissociation region.

$$T_0 = T^0 = 275\ \text{K}\,,\quad P_0 = 6 \cdot 10^6\ \text{Pa}\,,\quad P^0 = 2.5 \cdot 10^6\ \text{Pa}\,,\quad k = 10^{-17}\ \text{m}^2\,,\quad m = 0.2\,,\quad \lambda_s = 2\ \text{W/(m·K)}\,,$$

$$\lambda_w = 0.684\ \text{W/(m·K)}\,,\quad \lambda_h = 2.11\ \text{W/(m·K)}\,,\quad C_s = 10^3\ \text{J/(kg·K)}\,,\quad C_h = 2.5 \cdot 10^3\ \text{J/(kg·K)}\,,$$

$$C_w = 4.39 \cdot 10^3\ \text{J/(kg·K)}\,,\quad \rho_s = 2 \cdot 10^3\ \text{kg/m}^3\,,\quad \rho_w = 10^3\ \text{kg/m}^3\,,\quad \rho_h = 10^3\ \text{kg/m}^3\,,$$

$$q = 2.19 \cdot 10^6\ \text{J/kg}\,,\quad \mu_g = 10^{-5}\ \text{Pa·sec}\,,\quad R = 520\ \text{J/(kg·K)}\,,\quad \mu_w = 2 \cdot 10^{-3}\ \text{Pa·sec}\,.$$

In this case, the temperature of the hydrate ahead of the phase-transition front is lower than the dissociation temperature calculated from the pressure distribution while the temperature on the decomposition front is higher than the crystallization temperature of water.

The improvement in the permeability of the stratum qualitatively alters the solution. Figure 1b presents calculation results for $k = 5 \cdot 10^{-17}$ m^2 when the decomposition temperature of the hydrate in the region ahead of the dissociation front decreased below the temperature of the stratum, which indicates the superheating of the hydrate in this region. In this case, an extended region of decomposition of the hydrate analogous to that introduced in [1] occurs.

The pressure decrease at the boundary ($P^0 = 1.3 \cdot 10^6$ Pa) for the permeability $k = 10^{-17}$ m^2 leads to the intensification of the process of dissociation, and in this case the influx of heat to the front will not suffice for the dissociation temperature to be held in the region of positive temperatures (Fig. 1c). The dissociation temperature of the front calculated in the process of solution turns out to be lower than the water-crystallization temperature. Here the mathematical model also contains thermodynamic inconsistency, and it is natural to assume that in this case the process of decomposition of the hydrate occurs with the formation of ice [3–5].

If the pressure gradient and the permeability are rather high ($P^0 = 1.5 \cdot 10^6$ Pa, $k = 2 \cdot 10^{-17}$ m^2), one can carry out a dissociation regime where the superheating of the hydrate in the region ahead of the front is realized and simultaneously the temperature on the front lies below the crystallization temperature of the water (Fig. 1d). In this case, the physical process occurs with the formation of an extended region of dissociation and an ice-containing region, and for an adequate mathematical description we must introduce five regions of dissimilar thermodynamic states of a heterogeneous mixture (gas–hydrate, gas–water–hydrate, gas–ice–hydrate, gas–ice, and gas–water) divided by four boundaries of phase transitions.

It is of interest to consider the regions of the parameters for which one regime or another is realized. Figure 2 presents two neutral curves on the plane (k, P^0) that divide the plane into four regions in which the corresponding form of the solution is realized. In region 1, we have a consistent front solution. Region 2 corresponds to the existence of the solution with the formation of an ice-saturated zone, while region 3 corresponds to both the formation of an extended dissociation zone and the occurrence of ice. In the range of parameters corresponding to region 4, the hydrate dissociates in the extended zone at positive temperatures.

The change in the remaining parameters of the physical system leads to a change in the range of the parameters of realization of one or another regime and accordingly to the deformations of the critical curves. Thus, for example, as the stratum temperature increases, the existence domain of solutions with the formation of ice decreases, while as the initial pressure increases, the front regime becomes stabilized and its existence domain is extended. It is obvious from the critical diagram (Fig. 2) that ice can be formed in strata of rather high initial temperature if the permeability of the stratum and the pressure gradient are rather high, and this process is realized simultaneously with the formation of an extended dissociation region. The indicated parameter range corresponds to rather high permeabilities and pressure gradients and is beyond the framework of the approximation used in the present work.

This work was carried out with support from the Russian Foundation for Basic Research (project 99-01-00272).

NOTATION

ν, hydrate saturation; T, temperature; T_c, crystallization temperature of water; P, pressure; S, water saturation; v, filtration rate; f, relative permeability; m, porosity; k, permeability; C, heat capacity; R, gas constant; μ, viscosity; ρ, density; a, thermal diffusivity; λ, thermal conductivity; V, rate of jump; q, specific heat of dissociation; $\zeta = x/2\sqrt{a_1 t}$, dimensionless coordinate; $X(t) = 2\gamma\sqrt{a_1 t}$, law of displacement of the moving phase boundary; γ, dimensionless coefficient in the law of motion of the front; $\Theta_* = T_*/T_0$, dimensionless temperature; $\Pi_* = P_*/P_0$, dimensionless pressure. Subscripts: w, q, and s, water, gas, and skeleton of the porous medium respectively; h, hydrate; n, normal; + and –, quantities to the right and left of the front respectively; *, values of the quantities on the front; subscript 0, initial values; superscript 0, values at the stationary boundary; 1, ahead of the front; 2, behind the front.

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