Diffusion model of gas hydrate dissociation into ice and gas: Simulation of the self-preservation effect

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Valeriy A. Vlasov

Institute of the Earth Cryosphere, Siberian Branch of the Russian Academy of Sciences, P.O. Box 1230, 625000 Tyumen, Russian Federation

ABSTRACT

The diffusion model of gas hydrate dissociation into ice and gas is presented. This model takes into account the possible porous structure of the formed layer of ice as well as the intrinsic kinetics of the process of gas hydrate dissociation into ice and gas. Specifically, the problem of the dissociation of a spherical gas hydrate particle into ice and gas was considered. In the framework of a quasi-stationary approximation, a simplified solution to this problem was obtained. From the comparison between the calculated data obtained in the framework of a quasi-stationary approximation and the available experimental data, the parameters of the developed model responsible for the kinetics of methane hydrate dissociation into ice and gas were estimated. In the framework of the developed diffusion model, an explanation for the anomalous preservation thermal regime of gas hydrates is given. From this explanation it follows that for some hydrate-forming gases such a regime may not occur.

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1. Introduction

In the study of gas hydrates dissociation at temperatures below 273 K, their slow decomposition into ice and gas was detected [1,2]. This phenomenon is called the self-preservation effect. The self-preservation effect is attracting increasing interest because it can be the basis for the gas hydrate technologies for the long-term storage and transportation of various gases [3–5].

The self-preservation effect is being actively investigated [6–25]. This effect is observed during gas hydrates dissociation into ice and gas in the whole region of their thermodynamic instability at temperatures below the ice melting point. The self-preservation effect manifests itself not only in massive gas hydrates but also in disperse gas hydrates in some carrier medium [26–30]. The self-preservation effect is generally attributed to the formation of the ice layer on the gas hydrate surface. Depending on the temperature and pressure conditions, the ice layer may have a different degree of homogeneity. Herewith, the rate of gas hydrate dissociation into ice and gas is limited by the diffusion of the gas through this ever-increasing ice layer. It is obvious that the size effect will be the consequence of this dissociation mechanism: the larger the gas hydrate sample is, the longer it can exist in the thermodynamic instability region due to the self-preservation effect. The size effect is really manifested in experiments [31–33]. Moreover, the protective ice layer may appear after crystallisation of supercooled water,

which in turn may appear during the process of gas hydrate dissociation at temperatures below 273 K [34–38].

In works [39–42], methane hydrate dissociation into ice and gas at different fixed temperatures and a pressure of 0.1 MPa was investigated. These investigations revealed one feature: the rate of methane hydrate dissociation into ice and gas increases monotonically with increasing temperature in the range of 193–240 K. In the temperature range of 242–271 K, the anomalous preservation thermal regime (anomalous preservation effect) is observed: the rate of methane hydrate dissociation into ice and gas decreases noticeably and non-monotonically. According to the authors of works [39–41], for an explanation of the anomalous preservation thermal regime, it is not enough to assume that the rate of gas hydrate dissociation into ice and gas is limited only by the diffusion of the gas through the ice layer. In this case, the molecular processes occurring at the ice–hydrate interface may be important [16,19].

Presently, there is no full kinetic model of gas hydrate dissociation into ice and gas. In this paper, an attempt is made to create such a model. The presented model is based on the use of the diffusion equation, and when describing the processes occurring at the ice–hydrate interface, the general theory of chemical kinetics is used. Previously, such an approach has been used to create a kinetic model of gas hydrate formation from ice [43,44].

2. Theory

Assume that gas hydrate dissociation into ice and gas proceeds by the diffusion mechanism: the gas molecules G diffuse through

E-mail address: vlasov.ikz@gmail.com

the formed ice layer from the ice–hydrate interface on which the chemical reaction occurs

$$G + nH_2O(solid) \leftrightarrow G \cdot nH_2O, \tag{1}$$

where n is the hydration number. In the case under consideration, the rate of the forward reaction is lower than the rate of the reverse reaction. The thickness of the ice layer increases due to gas hydrate dissociation. Let us consider the situation in which the temperature at the front of the reaction (1) does not change during the process of gas hydrate dissociation. This situation is implemented under isothermal conditions in the case where the process of gas hydrate dissociation into ice and gas occurs rather slowly (even at the initial stage) or in the case where good thermal stabilisation exists. In both of these cases, the temperature at the front of the reaction (1) does not have time to change significantly, so we can assume that the process of gas hydrate dissociation into ice and gas occurs in the diffusion regime and should be considered only a diffusion problem.

Consider the problem of the dissociation into ice and gas of a single spherical gas hydrate particle with an initial radius R_0 (Fig. 1). During the process of gas hydrate dissociation, the radius of the gas hydrate core $\xi(t)$ decreases. We assume that during the process of gas hydrate dissociation, the outside radius of the ice layer $R(t)$ also decreases. Such a decrease can be due to the different densities of ice and the gas hydrate. Moreover, we assume that the particle under consideration is found in the atmosphere of the hydrate-forming gas at constant pressure p and constant temperature T. Herewith, the pressure of the hydrate-forming gas is less than the pressure of the ice–gas hydrate–gas equilibrium p_{eq}. Note that if gas hydrate dissociation into ice and gas occurs at a fixed temperature in the atmosphere of the non-hydrate-forming gas (as often occurs in real experiments), then it must be assumed that $p = 0$.

We formulate the problem in the spherical coordinate system by choosing its origin at the centre O of the particle under consideration. We take into account the possible presence of pores in ice by introducing the effective diffusion coefficient of the gas in ice:

$$D_{eff} = D + D_{por}, \tag{2}$$

where D is the diffusion coefficient of the gas in ice and D_{por} is the coefficient characterising the diffusion of the gas through the system of pores in ice. In this case, the diffusion equation is written as

$$\frac{\partial c(r,t)}{\partial t} = D_{eff}\left(\frac{\partial^2 c(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial c(r,t)}{\partial r}\right), \quad t > 0, \quad \xi(t) < r < R(t), \tag{3}$$

where $c(r,t)$ is the molar concentration of the gas in the ice layer, r is the radial coordinate, and t is the time.

The initial condition is written in the form

$$c(r,t)|_{t=0} = 0, \quad 0 \leqslant r < R_0. \tag{4}$$

Taking into account the fact that the molar concentration of the gas outside the particle under consideration is determined from its thermal equation of state, the external boundary condition is written as follows:

$$c(r,t)|_{r=R(t)} = \frac{p}{ZRT}, \quad t > 0, \tag{5}$$

where Z is the compressibility factor of the gas under current thermobaric conditions and R is the gas constant.

Gas molecules appear on the ice–hydrate interface due to reaction (1). Next, these molecules diffuse through the ice layer to the surface of contact of the particle under consideration with the gaseous phase. Thus, the internal boundary condition can be written as

$$r_g = j|_{r=\xi(t)}, \quad t > 0, \tag{6}$$

where r_g is the rate of change in the moles of the gas on the ice–hydrate interface and j is the magnitude of the molar flux of the gas in the ice layer. In the framework of the general theory of chemical kinetics, it can be shown [45] that the following relation is satisfied for the quantity r_g:

$$r_g = k_{dis}\chi\left(1 - \frac{Z_{eq}RT}{p_{eq}}c(r,t)|_{r=\xi(t)}\right), \quad t > 0, \tag{7}$$

where k_{dis} is the rate constant for the gas hydrate dissociation reaction at the ice–hydrate interface, χ is the molar density of the gas hydrate, and Z_{eq} is the compressibility factor of the gas under equilibrium conditions. The rate constant k_{dis} obeys the Arrhenius equation and characterises the intensity of the gas hydrate dissociation reaction on the ice–hydrate interface. The molar flux of the gas in the ice layer is defined as

$$\mathbf{j} = -D_{eff}\frac{\partial c(r,t)}{\partial r}\mathbf{e}_r, \quad t > 0, \quad \xi(t) < r < R(t), \tag{8}$$

where $\mathbf{e}_r$ is the radial unit vector. Taking into account Eqs. (7) and (8) and given that $r_g > 0$ and $\partial c(r,t)/\partial r < 0$, the internal boundary condition (6) is written in the form

$$k_{dis}\chi\left(1 - \frac{Z_{eq}RT}{p_{eq}}c(r,t)|_{r=\xi(t)}\right) = -D_{eff}\frac{\partial c(r,t)}{\partial r}\bigg|_{r=\xi(t)}, \quad t > 0. \tag{9}$$

Appendix A shows that there is the following interrelation between the quantities $R(t)$ and $\xi(t)$:

$$R(t) = \sqrt[3]{\frac{\chi M_h(1-\varepsilon_h)}{\omega M_w(1-\varepsilon_i)}\left(1 + \frac{M_g}{nM_w}\right)^{-1}\left(R_0^3 - \xi^3(t)\right) + \xi^3(t)}, \quad t \geqslant 0, \tag{10}$$

where ω is the molar density of ice; M_w, M_h and M_g are the molar masses of water, the gas hydrate and the gas, respectively; and ε_i and ε_h are the porosities of ice and the gas hydrate, respectively.
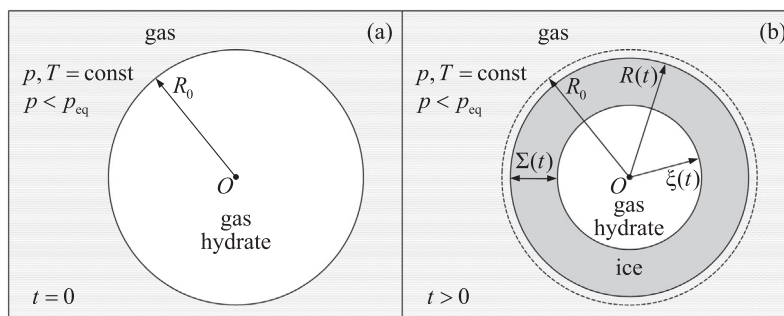

Fig. 1. Geometry of the problem at (a) the initial time and (b) later times.