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Diffusion Theory of Formation of Gas Hydrate from Ice Powder without Melting

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Abstract

Based on the single ice particles shrinking core model, the authors simulated the kinetic of gas hydrates formation from ice powders by the improved rate of volume ice-to-hydrate transformation that considered the volume expansion and consolidation of the sample during hydrate formation. The comparsion of the degree of hydrate formation between the calculated and the measured was conducted. Gas hydrates grown at gas-ice interfaces were a submicron porous structure. The pore structure provides the diffusion for gas molecules through the hydrate shell in reactions. And the diffusion plays an important role in this process of the reaction. In comparison with the experimental data, the reasonability of the model is verified. The curve of the reaction degree with time in different temperatures and initial pressures calculated in this paper by our programs has a good agreement with measured value.

1. Introduction

Methane hydrate is a nonstoichiometric compound consisting of a network of H_2O molecules that are hydrogen-bonded in a manner similar to ice and interstitially encaging CH_4 gas molecules[1]. Experiments show that hydrate formation rate from ice is faster than other methods, typically, the gas content of unit volume is higher than hydrate formation from water. Therefore, the research of the formation form ice is valuable for hydrate storage and transportation technology [2].

In the exploration of hydrate formation mechanism from ice, the gas hydrates grown at gas-ice interfaces were examined by electron microscopy and found to have a submicron porous structure [3,4,5] Doroteya K. Staykova et al. proposed a multistage model which is validated by experiments[6]. This model described the formation mechanism excellently. The description of the model depends heavily on experimental parameters. V. A. Vlasov proposed phenomenological diffusion theory [7]. This model was considered as the variation of the effective diffusion coefficient with time, which was caused by pore structure changes over time in hydrate layer.

Based on the single ice particles shrinking core model [8], referring to V. A. Vlasov's mathematical model of diffusion theory [7] and Staykova, Salamatin et.al's theory [6], the authors try to construct a novel diffusion model which makes the use of parameters that is easy to get from experiments.

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2. Theoretical Model

2.1 Theoretical Basis

In the single ice particles shrinking core gas-solid reaction model [8, 9], a spherical ice particle is selected as the research object. A certain concentration of gas molecules is outside of ice particle, and gas molecules in the surface layer of ice particles firstly generate a thin hydrate coating by clathrate reaction. Since the lesser density of water in the porous hydrate phase, hydrate layer is expanding outward. According to the relationship of hydrate reaction kinetics equation and the concentration (which can be obtained by pressure change and gas balance equation), a dynamic balance equation on the reaction interface can be established. Combined with the equation established by the movement of reaction can deduce the function relationship of geometry radius and reaction time. The authors combined the intrinsic reaction kinetics equations that deem the residual pressure (the difference between environmental pressures and the decomposition pressure) as the driving force with equations of chemical kinetics, and pressure change function of reaction can be obtained by the experimental data fitting. Gas diffusion coefficient in hydrate layer can be calculated via the relationship between the penetration rate constant with diffusion coefficient.
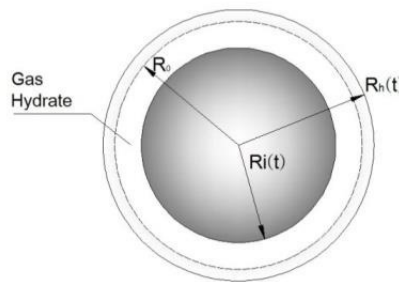

Fig. 1. Geometry of problem of formation of gas hydrate from spherical ice particle with initial radius R_0.

2.2 Formula and programs

The formula and programs are seen in Appendix A. The formula (19) makes it workable that calculating the diffusion coefficient value firstly and then gradually substituting into formula (17) (14) (22) (13) to calculate geometry values and the degree of hydrate formation. And the nomenclature is in Appendix B. Iterative method is used to programme and calculate. Processes in detail are in Appendix A.

3. Results and discussion

The experimental device can accurately control the parameters of the reaction system, such as temperature，pressure, and measures continuous and records automatically by IPC and D/A module. Open the high pressure reactor when the temperature of bath was stable, and pour ice powder particles which had uniform particle diameter. Purge and vacuumize the pipeline slowly, and pump methane gas to pressure required for the experiment. Close the valve to check the system for leaks. The transformation of temperature and pressure in system can be obtained by data acquisition module. Since the formation of gas hydrates from ice powders is a solid-reaction process, the amount of gas consumption and hydrate formation can be calculated according to the gas state equation.

In Fig. 2, it shows that the reaction rate is more sensitive to temperature when the temperature is close to freezing point. In the early stages of the reaction, the reaction rate constant of gas hydrate on the surface in higher temperature is higher, and the formation rate is higher too. The diffusion coefficient relevant with structure is demonstrated in Fig.3 (a). It revealed that in the beginning time, diffusion resistance is not obvious in the beginning time though the diffusion coefficient is small. In the initial stage, ice particle surface is involved by high concentrations of gas composition and the reaction is dominated by clathrate reaction limit instead of diffusion limit. With the degree of hydrate formation increasing,
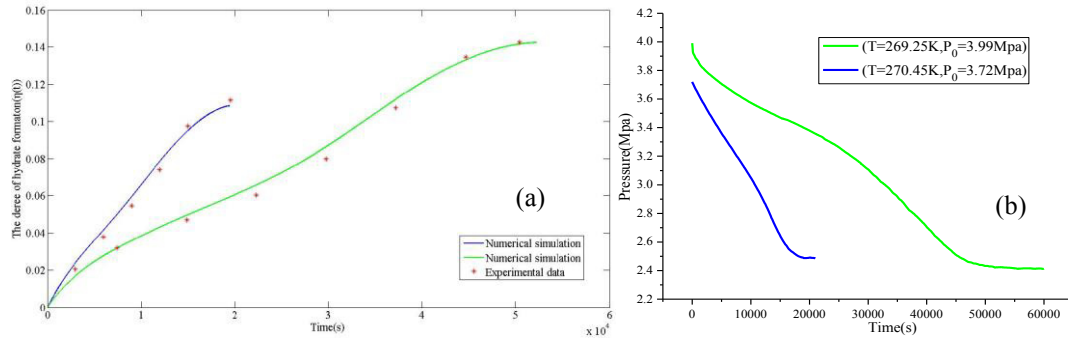
Fig. 2.(a) The curves of the degree of hydrate formation(The mass conversion rate of ice); (b) The obtained curves of pressure drop history in experiments.

In Fig.2, the blue line is in T=270.45K, P_0=3.72Mpa, k_{R1}=4×10^{-35}$m^{18.25}$/(mol$^{5.75}$s), k_{R2}=0.008511$mol/(m^2s)$; The green line is in T=269.25K, P_0=3.99Mpa, k_{R1}=3×10^{-35} $m^{18.25}$/(mol$^{5.75}$s), k_{R2}=0.007716$mol/(m^2s)$; the average diameter of ice particles are 380μm.
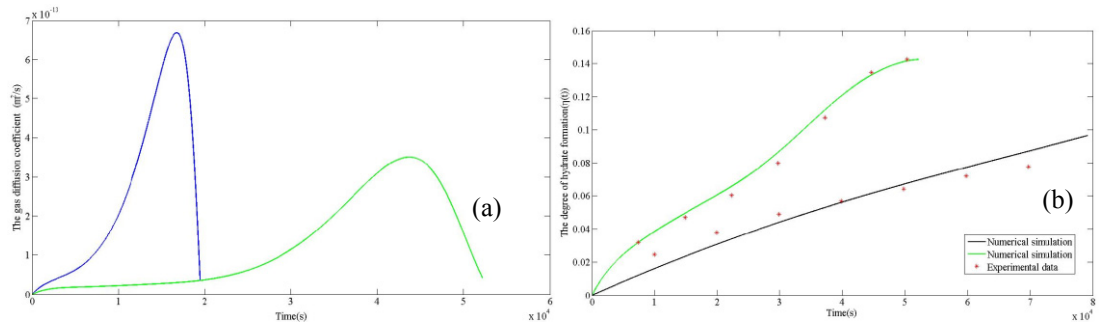

Fig. 3. (a) The curve of gas diffusion coefficient;   (b) The curves of the degree of hydrate formation(The mass conversion rate of ice).

In Fig.3, the green line is in T=269.25K, P_0=3.99Mpa, k_{R1}=3×10^{-35} $m^{18.25}$/(mol$^{5.75}$s), k_{R2}=0.007716$mol/(m^2s)$; the black line is in T=264.85K, P_0=9.32Mpa, k_{R1}=4×10^{-37}$m^{18.25}$/(mol$^{5.75}$s), k_{R2}=0.005345$mol/(m^2s)$ and has a total reaction time of 120 h and a higher finally conversion rate. The average diameter of ice particles are 380 μm.
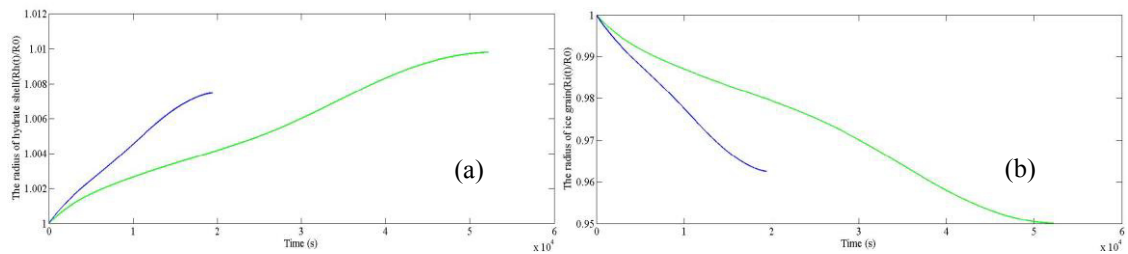

Fig.4. (a) The curve of the outside radius of the gas hydrate layer ($R_h(t)$/ R_0); (b) The curve of the inside radius of ice ($R_i(t)$/ R_0).

the hydrate layer coating ice particle is formed and its thickness is gradually grew. The armor of hydrate shell hinders gas permeation into the ice surface inside. The diffusion coefficient of gas in the hydrate is, at least two orders of magnitude, less than those in ice [10]. Hydrate growth rate gradually flatten out and it is demonstrated in Fig.2 (b) that the pressure didn't go down finally. Experiments show that at the end of the reaction, gas pressure is much higher than the equilibrium pressure in that temperature (for example, at 270.15K, the residual pressure is 0.4Mpa). At this very moment, if the temperature is constant, only

increasing the driving force or pore pressure can drive adequate gas into reaction surface and stimulate the reaction. So Green-curve (Fig.2 (a)) that has higher initial pressure has longer reaction time and higher percent conversion.

From the perspective of a curve trend, the formation rate has a brief increase during reaction. The simulation has not count for the exothermic reaction of hydrate formation. But it is a speculation that this heat accumulation in hydrate layer should prompt the reaction rate after a period of initial reaction.

4. Conclusions

The reaction rate constant for formation of gas hydrate on the surface is more sensitive to temperature when the temperature is close to freezing point [11]. The higher temperature can also increase the diffusion ability that in turn can promote the reaction. However, with the increasing thickness of hydrate layer, diffusion resistance increases obviously to hinder the reaction. In short, temperature influences reaction rate, and pressure determines the extent of reaction. In order to obtain higher conversion rate, supplementing pressure timely and increasing reaction temperature reasonably is needed. Moreover, reducing the ice particle diameter to increase the specific surface area and the reaction interface area can also improve the conversion rate.

Acknowledgements

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Biography

Weiguo Liu was born in Shandong, China and completed his PhD at Dalian University of Technology. He is currently Associate Professor at Dalian University of Technology and his interesting fields are focus on the methane hydrate formation kinetics and the mechanical properties of hydrate-bearing sediments.

Appendix A.

Based on the single ice particles shrinking core gas-solid reaction model[9]，Select spherical ice particles as the research object, and radial Laplace operator Δr was introduced.

In order to describe the impact of constantly hydrate layer getting thicker, diffusion coefficient was represented as follows:

$$D_{eff} = D(t,*) \ , \tag{1}$$

* represented for the transformation of effective diffusion coefficient with the structure or the time. Correspondingly, diffusion equation can be written as:

$$\frac{\partial c(r,t)}{\partial t} = D_{eff}(t)\Delta_r c(r,t), \ t > 0, R_i(t) < r < R_h(t) \ , \tag{2}$$

For the reaction in spherical radial, the specific expression was:

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

In the initial moments,

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

Boundary conditions of the outer surface of hydrate shell were:

$$c(r,t)|_{r=R_h(t)} = \frac{p}{Z(p,T)\text{RT}}, \ t > 0 \tag{5}$$

Reaction equation occurring on the interface of the hydrate and ice was written as:

$$G + nH_2O(solid) \leftrightarrow G \cdot nH_2O \tag{6}$$

According to the theory of chemical reaction kinetics [6, 8, 11], the rate of increase in the amount of the gas hydrate on the surface was written as:

$$\omega_h = k_{R1} \rho_{mi}{}^n \left(c(r,t)|_{r=R_i(t)} - \frac{P_{eq}}{Z(P_{eq},T)RT} \right), t > 0 \tag{7}$$

Based on Arrhenius-type equation, k_{R1} is a function of temperature. The authors did not find the reference where the function of k_{R1} with temperature T and chemical activation energy is founded when methane hydrate generate from ice powder below freezing point. Therefore, this article estimate a value which is is observed good agreement of experimental and calculated data and take the following formula as references[11]

$$lnk_R = lnk_0 - \frac{E}{RT} ,$$
$$lnk_0 = -49.9 \pm 3.3 (m^{18.25}/(mol^{5.75}s)) , E = 63.8 \pm 7.5kJ/mol ,$$

While the rate of decrease in the amount of the gas on the surface during a chemical reaction was expressed as:

$$\omega_g = -\omega_h \tag{8}$$

The following formula is formed on the reaction surface(The inside surface of hydrate shell):

$$D_{eff}(t) \frac{\partial c(r,t)}{\partial r}|_{r=R_i(t)} = -\omega_g = k_{R1} \rho_{mi}{}^n \left(c(r,t)|_{r=R_i(t)} - \frac{P_{eq}}{Z(P_{eq},T)RT} \right) \tag{9}$$

According to the principle of mass conservation, there was the following equation:

$$m_h(t) = m_i'(t) + m_g'(t) \tag{10}$$

According to hydrate structure, a gas molecule goes with n water molecules:

$$n \frac{m_g'(t)}{M_g} = \frac{m_i'(t)}{M_w} \tag{11}$$

The reacted ice mass was:

$$m_i'(t) = \frac{m_h(t)}{1+\frac{M_g}{nM_w}} \tag{12}$$

The degree of hydrate formation is numerically equal to the mass fraction of ice that passed into the structure of a gas hydrate as follows:

$$\eta(t) = \frac{m_i'(t)}{m_{i0}} = \frac{m_h(t)}{m_{i0}(1+\frac{M_g}{nM_w})}, t \geq 0 \tag{13}$$

$$m_{i0} = \frac{4}{3}\pi N\rho_i R_0^3, \ m_h = \frac{4}{3}\pi N\rho_h(R_h^3(t) - R_i^3(t))$$

From (10) (11) (12) (13), the following equations can be deduced:

$$R_h(t) = R_0 \sqrt[3]{1 - \eta(t) + \frac{\rho_i}{\rho_h}\left(1 + \frac{M_g}{nM_w}\right)\eta(t)} =$$

$$\sqrt[3]{\frac{\rho_{mi}M_w}{\rho_{mh}M_h}\left(1 + \frac{M_g}{nM_w}\right)(R_0^3(t) - R_i^3(t)) + R_i^3(t)}, t \geq 0 \tag{14}$$

In case of the infinitesimal time and tiny concentration change of gas, $\frac{\partial^2 c(r,t)}{\partial r^2} + \frac{2}{r}\frac{\partial c(r,t)}{\partial r} = 0$ was founding. And from (3)、(9)，the simplified solution was following:

$$c(r,t) = \frac{P}{Z(P,T)RT}\frac{D_{eff}+k_{R1}\rho_{mi}{}^n R_i(t)\left(1-\frac{R_i(t)}{r}\right)}{D_{eff}+k_{R1}\rho_{mi}{}^n R_i(t)\left(1-\frac{R_i(t)}{R_h(t)}\right)} + \frac{P_{eq}}{Z(P_{eq},T)RT}\frac{k_{R1}\rho_{mi}{}^n R_i^2(t)\frac{R_h(t)-r}{R_h(t)r}}{D_{eff}+k_{R1}\rho_{mi}{}^n R_i(t)\left(1-\frac{R_i(t)}{R_h(t)}\right)}, t >$$

$$0, R_i(t) < r < R_h(t) \tag{15}$$

The moving equation of reaction boundary was:

$$\frac{dR_i(t)}{dt} = \frac{\omega_g}{\rho_{mi}} = -\frac{n\omega_h}{\rho_{mi}} = nk_{R1}\rho_{mi}{}^{n-1}\left(\frac{P_{eq}}{Z(P_{eq},T)RT} - c(r,t)|_{r=R_i(t)}\right) \tag{16}$$

Put the (15) into (16), (16) can be written again as follows:

$$\frac{dR_i(t)}{dt} = \frac{-nD_{eff}k_{R1}\rho_{mi}^{n-1}R_i(t)\delta}{D_{eff}+k_{R1}\rho_{mi}^{n}R_i(t)(1-\frac{R_i(t)}{R_h(t)})}, t > 0 \tag{17}$$

$$\delta = \frac{P}{Z(P,T)RT} - \frac{P_{eq}}{Z(P_{eq},T)RT}$$

The amount of substance of the gas can be described by the real gas state equation:

$$\upsilon = \frac{pV}{ZRT} \tag{18}$$

Since the reaction occurs at the surface of the ice core, ω_h can be expressed by follows[6]:

$$\omega_h = \frac{n\Delta\upsilon}{N\cdot 4\pi R_i^2(t)} = \frac{K_{R2}k_D}{K_{R2}+k_D}ln\frac{p}{p_{eq}} \tag{19}$$

According to the diffusion put forward by Crank [12], k_D satisfied the following formula:

$$\frac{1}{k_D} = \frac{R_i^2(t)}{\rho_{mh}D_{eff}}\left(\frac{1}{R_i(t)} - \frac{1}{R_h(t)}\right) \tag{20}$$

When pressure is a function of time, the following equations can be obtained:

$$p = p(t) \tag{21}$$

$$\upsilon(t) = \frac{p(t)V(t)}{ZRT}, \ V(t) = V_B - N\frac{4}{3}\pi R_h^3(t) \tag{22}$$

In the initial time, $k_D >> k_{R2} >> 1$，the following equation can be written:

$$\omega_h = k_{R2}ln\frac{p_0}{p_{eq}}$$

By estimating the initial time of hydrates covering ice particles (δ_t), the initial thickness of hydrate layer can be obtained:

$$\delta_r = k_{R1}\rho_{mi}{}^n \frac{P_0}{ZRT}\frac{\delta_t}{\rho_{mh}} \tag{23}$$

p(t) can be obtained by experimental data. Firstly, an initial film thickness can be obtained by the formula (23). For sufficiently small discrete time intervals, solve the formula (17) on the current time. Then the solution was substituted into (14) (22), and D_{eff} can be calculated. For the next iteration, the following approximate relationship can be used:

$$D_{eff}{}^{t+dt} = D_{eff}{}^t \tag{24}$$

Appendix B.

c is the gas concentration in the bulk of the gas phase, mol/m^3;

$c(r, t)$ is the gas concentration in the layer of the gas hydrate, mol/m^3;

D_{eff} is the effective diffusion coefficient of the gas in the gas hydrate that does not depend on time, m^2/s;

k_{R1} is the reaction rate constant for formation of gas hydrate on the surface in chemical kinetics , $m^{3n+1}/(mol^n \cdot s)$;

k_{R2} is the reaction rate constant for formation of gas hydrate in kinetics model, $mol/(m^2 \cdot s)$;

E is activation energy of the gas hydrate formation reaction at interface, J/mol;

k_D is the penetration rate constant, $mol/(m^2 \cdot s)$;

M is molar mass, kg/mol;

$m'_g(t)$ is the total mass of the gas that passed into the structure of the gas hydrate, kg;

$m_h(t)$ is the mass of the gas hydrate in the sample, kg;

$m'_i(t)$ is the total mass of ice that passed into the structure of the gas hydrate, kg;

m_{io} is the initial mass of ice in the sample, kg;

N is the number of ice particles in the sample;

P is the gas pressure outside the particle, Pa;

P_0 is the initial reaction pressure, Pa;

P_{eq} is the pressure of the ice–gas hydrate–gas equilibrium, Pa;

R is the gas constant, $J/(mol \cdot s)$;

$Rh(t)$ is the outside radius of the gas hydrate layer, m;

R_0 is the initial radius of the ice particle, m;

r is the radial coordinate, m;

ω_g is the rate of decrease in the amount of the gas on the surface during a cage-reaction, $mol/(m^2 \cdot s)$;

ω_h is the rate of increase in the amount of the gas hydrate on the surface during a chemical reaction(the rate of volume ice-to-hydrate transformation), $mol/(m^2 \cdot s)$;

T is the temperature, K;

t is the time, s;

$V_{h(t)}$ is the volume of the gas hydrate layer, m^3;

V_{io} is the initial volume of the ice particle, m^3;

$Z(P,T)$ is the compressibility factor;

$Z(P_{eq},T)$ is the compressibility factor for a gas that is under equilibrium conditions;

$\eta(t)$ is the degree of hydrate formation(the mass conversion rate of ice);

v is the amount of substance, *mol*;

Δv variable quantity the amount of substanceof in unit interval, mol/s;

$R_i(t)$ is the inside radius of the gas hydrate layer, m;

ρ_i is the mass density of ice, kg/m^3;

ρ_h is the mass density of hydrate, kg/m^3;

ρ_{mh} is the molar density of hydrate, mol/m^3;

ρ_{mi} is the molar density of ice, mol/m^3;

V_B is the volume of vessel, m^3;

δ_t is micro value for computing needs of model, s; And in this paper, it is $0.1s$.