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Physical and Chemical Properties of Gas Hydrates: Theoretical Aspects of Energy Storage Application

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A model has been developed permitting to accurately predict on molecular level phase diagram of the clathrate hydrates. This model allows to take into account the influence of guest molecules on the host lattice and to extend the interval of temperatures and pressures of computed thermodynamic potentials and significantly improves known van der Waals and Platteeu theory. The theoretical study of phase equilibrium in gas–gas hydrate–ice Ih system for methane and xenon hydrates has been performed. The obtained results are in a good agreement with experimental data. A new interpretation of so-called self-preservation effect has been proposed. The self-preservation of gas hydrates can be connected with differences in thermal expansions of ice Ih and gas hydrates. This is confirmed by calculations performed for methane and mixed methane–ethane hydrates. [doi:10.2320/matertrans.48.704]

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1. Introduction

Although fossil and nuclear sources will remain the most important energy provider for many more years, flexible technological solutions that involve alternative means of energy supply and storage need to be developed urgently. Natural gas hydrates have attracted considerable interest as globally distributed deposits harboring potential hydrocarbon reserves on Earth, which are considered as a potential energy resource in the future.^{1,2)} In recent years, hydrogen hydrates have been the focus of attention as the storage of large quantities of hydrogen after report that the structure of hydrogen hydrate with CS-II structure can store around 4.96–5.3 weight% of hydrogen at 220 MPa and 234 K.^{3,4)} Hydrogen hydrates save at ambient pressure and 77 K and decompose and release hydrogen at 140 K. Ice-like hydrogen-bonded structures of clathrate hydrates formed by water molecules arranging themselves in a cage-like structure around guest molecules can contain several hundred times their own volume in gas. For instance, hydrogen clathrate hypothetically contains 500 times its volume in H₂ gas (under standard conditions 0.1 MPa and 273 K) while stable at 145 K at a pressure 0.01 MPa. As usual the cages of hydrate clathrate structures cubic structures I (CS-I), II (CS-II) and hexagonal (H) fit for an individual guest molecule, but these cages are much too large for an individual H₂ molecule, and therefore, the existence of hydrogen hydrate with single cage occupancy was not suspected.

Natural gas hydrates are being studied worldwide as transport manufactured materials as they are more suitable for large-scale transport of natural gas over long distances than liquefied natural gas. A main component of hydrate deposits is methane hydrate formed from water and methane molecules so the hydrocarbon gas mixture contains >99% methane.^{1,2)}

Many experimental studies were focused on the consid-

erably delayed dissociation of gas hydrate at 1 atm. (the so-called self-preservation effect) above equilibrium temperature for hydrate breakdown, but below the H₂O ice point.^{5–19)} The anomalous preservation of methane hydrate observed below the melting point of ice at 242–271 K^{13,17)} has potential application for temporary low-pressure transport, storage of natural gas and developing safe, dependable technologies to produce natural gas from methane hydrates. Recently, research of the preservation in pure methane and methane–ethane hydrates have shown extremely nonlinear temperature-dependence of methane hydrate dissociation behavior and the utter lack of comparable preservation behavior in CS-II methane–ethane hydrate.^{13,17)} The large temperature differences (up to 30 K) between sample interiors and surroundings were observed in the time of methane hydrate rapid (endothermic) dissociation.¹⁷⁾ The experimental research showed the ice phase formation during dissociation of gas hydrate and existent thermal gradients between sample interiors and surroundings. As it was shown in^{13,15,17)} the macroscopic ice-shielding model does not explain anomalous preservation up to 93% of methane hydrate. The mechanism of the anomalous preservation behavior of gas hydrate is not clear and needed further investigation.

Without contradictions with experiment we will suggest that at the first stage of dissociation of gas hydrate the ice phase including gas hydrate phase with temperature lower than that of the surrounding temperature with subsequent establishment of temperature balance. Increasing of is occurring inside methane hydrate under increasing temperature, and if the ice structure does not breakdown, the methane hydrate may have larger pressure than ice phase. This is due to the fact that the thermal expansion of methane hydrate is a few times larger than ice one. Great attention was focused on the thermal expansion of clathrate hydrates because it was found to be considerably larger than for the hexagonal ice.¹⁾ Molecular dynamics (MD) calculations of the thermal expansion of ice and structure I ethylene oxide

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hydrate²⁰) and structure II krypton hydrate²¹) have shown that the linear expansion coefficients of hydrates are greater than in the hexagonal ice. The lattice dynamic (LD) calculations also give larger values of thermal expansion of gas hydrates than that of the ice.^{22–24}

For practical application of clathrate hydrates as storage materials, it is important to know the region of stability of these compounds (there are several type of gas hydrate structures with different cage shapes) at various pressure and temperatures. Currently, analytical theories of clathrate compounds, which allow one to construct the T-P diagram of gas hydrates, are still based on the pioneering work of van der Waals and Platteeuw. This theory and all of its subsequent derivatives embody four main assumptions. Three of which are that (a) cages contain at most one guest; (b) guest molecules do not interact with each other; and (c) the host lattice is unaffected by the nature as well as by the number of engaged guest molecules are clearly violated in the case of hydrogen clathrates which show multiple occupancy. Dyadin and Belosludov have shown how a non-ideal solution theory can be formulated to account for guest-guest interaction.²⁵ In other studies, Westcott & Rodger have shown how the lattice dynamics (LD) formalism that has proved so successful in numerical simulations of gas hydrate properties can be simplified to allow for full free-energy optimization calculations for equilibrium properties.²⁶ A generalization of

the van der Waals–Platteeuw (vdW–P) statistical thermodynamic model of clathrate hydrates, applicable for arbitrary multiple filling the cages, is formulated in²⁷) and.²⁸) However, these developments do not go far enough, and a much more comprehensive theory is desperately needed. Therefore, we will develop a statistical thermodynamic theory of clathrate hydrates that accounts for the mutual influence of guest and host molecules (non-rigid host lattice) and guest-guest interaction—especially when more than one guest molecule occupies a cage. Using this theory we study the structure, thermodynamic properties and pressure of hydrate phases immersed in the ice phase with the aim to understand the existence of self-preservation effect in different clathrate hydrate. The validity of the proposed approach will be checked for methane and xenon hydrates and results will be compared with known experimental data.

2. Theory

Our subsequent development of a model is based only on one of the assumptions of van der Waals–Platteeuw theory: the contribution of guest molecules to the free energy is independent of mode of occupation of the cavities at a designated number of guest molecules. This assumption allows to separate the entropy part of free energy.²⁹)

$$F = F_1(V, T, y_{11}^1, \dots, y_{nm}^k) + kT \sum_{t=1}^m N_t \left[\left(1 - \sum_{l=1}^n \sum_{i=1}^k y_{lt}^i \right) \ln \left(1 - \sum_{l=1}^n \sum_{i=1}^k y_{lt}^i \right) + \sum_{l=1}^n \sum_{i=1}^k y_{lt}^i \ln \frac{y_{lt}^i}{i!} \right] \quad (1)$$

where F_1 is the part of the free energy of clathrate hydrate for the cases when some types of cavities and guest molecules exist, and a cavity can hold more than one guest molecule. The second term is the entropy part of free energy of a guest system, $y_{lt}^i = N_{lt}^i/N_t$ —the degree of filling of t -type cavities by i cluster of l -type guest molecules; N_t —number of t -type cavities; N_{lt}^i —number of l -type guest molecules which located on t -type cavities and united in i -clusters.

At given arrangement $\{y_{11}^1, \dots, y_{nm}^k\}$ of the clusters of guest molecules in the cavities the free energy $F_1(V, T, y_{11}^1, \dots, y_{nm}^k)$ of the crystal can be calculated within the framework of a lattice dynamics approach in the quasiharmonic approximation^{30,31}) as

$$F_1(V, T, y_{11}^1, \dots, y_{nm}^k) = U + F_{vib} \quad (2)$$

where U is the potential energy, F_{vib} is the vibrational contribution:

$$F_{vib} = \frac{1}{2} \sum_{\vec{q}} \hbar \omega_j(\vec{q}) + k_B T \sum_{\vec{q}} \ln(1 - \exp(-\hbar \omega_j(\vec{q})/k_B T)) \quad (3)$$

where $\omega_j(\vec{q})$ is the j -th frequency of crystal vibration and \vec{q} is the wave vector.

Our model based on the possibility of calculation of free energy while accounting for the energy of interaction of guest molecules and the host lattice. Equation of state can be found by numerical differentiation of free energy:

$$P(V, T) = - \left(\frac{\partial F(V, T, y_{11}^1, \dots, y_{nm}^k)}{\partial V} \right)_0 \quad (4)$$

The “zero” index mean constancy of all thermodynamic parameters except the ones which differentiation execute. After reception, we can calculate the free energy values μ_{lt}^i —the chemical potentials of i -clusters of l -type guest molecules which are located on t -type cavities and μ_Q —the chemical potential of host molecules:

$$\mu_{lt}^i(P, T, y_{11}^1, \dots, y_{nm}^k) = \left(\frac{\partial F(V(P), T, y_{11}^1, \dots, y_{nm}^k)}{\partial N_{lt}^i} \right)_0 = \frac{\partial F_1(V(P), T, y_{11}^1, \dots, y_{nm}^k)}{\partial N_{lt}^i} + kT \ln \frac{y_{lt}^i}{i! \left(1 - \sum_{l', i'} y_{l't'}^{i'} \right)} \quad (5)$$

$$\mu_Q(P, T, y_{11}^1, \dots, y_{nm}^k) = \frac{1}{N_Q} \left\{ [F(V(P), T, y_{11}^1, \dots, y_{nm}^k) + PV(P)] - \sum_i^k \sum_{l=1}^n \sum_{t=1}^m N_{lt}^i \mu_{lt}^i \right\} = \frac{PV(P)}{N_Q}$$

$$+ \frac{1}{N_Q} F(V(P), T, y_{11}^1, \dots, y_{nm}^k) - \frac{1}{N_Q} \sum_{t=1}^m \sum_{l=1}^n \sum_{i=1}^k N_{lt}^i \frac{\partial F_1(V(P), T, y_{11}^1, \dots, y_{nm}^k)}{\partial N_{lt}^i} + kT \sum_{t=1}^m v_t \ln \left(1 - \sum_{l'} \frac{n_{l'}^i}{V} \right) \quad (6)$$

The derivative can be found by numerical calculation using the following approximation:

$$\left(\frac{\partial F_1(V(P), T, y_{11}^1, \dots, y_{nm}^k)}{\partial N_{lt}^i} \right)_0 \cong \frac{F_1(V(P), T, N_{11}^1, \dots, N_{lt}^i, \dots, N_{nm}^k) - F_1(V(P), T, N_{11}^1, \dots, N_{lt}^i - N_{lt}^i n_{lt}^i, \dots, N_{nm}^k)}{N_{lt}^i n_{lt}^i} \quad (7)$$

where $N_{lt}^i n_{lt}^i$ is number of clusters of guest molecules removed from clathrate hydrate.

We are concerned with the monovariant equilibrium of the gas phase, ice and clathrate hydrate. The curve $P(T)$ of monovariant equilibrium can be found from the equality of the chemical potentials of the system components in the phases:

$$\mu_{lt}^i(P, T, y_{11}^1, \dots, y_{nm}^k) = i\mu_{lt}^{gas}(P, T) \quad (8)$$

$$\mu_Q(P, T, y_{11}^1, \dots, y_{nm}^k) = \mu_Q^{ice}(P, T) \quad (9)$$

The curve $P(T)$ of divariant equilibrium can be found at the fixed degree of filling y_{lt}^i from eq. (9). We shall assume that the ideal gas laws govern the gas phase, and then the expressions for chemical potentials of mixture components will be as following:

$$\mu_{lt}^{gas}(P, T) = kT \ln [x_l P / kT \Phi_l] = kT \ln \left[x_l \frac{P}{kT} \left(\frac{2\pi\hbar^2}{m_l kT} \right)^{3/2} \right] \quad (10)$$

where x_l the mole fraction of the l -type guest in the gas phase. In addition, we neglect the water vapor pressure.

Here we shall deal with clathrate hydrate which has two types of cavities and one type of guest and a cavity can hold one guest molecule only. The curve $P(T)$ of monovariant equilibrium described by the following eqs. (8), (9) govern:

$$\begin{aligned} \mu_Q(P, T, y_1, y_2) \cong & +F(V(P), T, y_1, y_2)/N_Q - \frac{\partial F_1(V(P), T, y_1, y_2)}{N_Q \partial y_1} - \frac{\partial F(V(P), T, y_1, y_2)}{N_Q \partial y_2} \\ & + \frac{PV(P)}{N_Q} + kT(v_1 \ln(1 - y_1) + v_2 \ln(1 - y_2)) = \mu_Q^{ice}(P, T) \end{aligned} \quad (11)$$

$$\begin{aligned} y_1 = & \left[1 + \exp \left(\frac{F_1(V(P), T, y_1, y_2) - F_1(V(P), T, y_1(1 - n_1), y_2)}{N_1 y_1 n_1 kT} - \mu^{gas}(P, T)/kT \right) \right]^{-1} \\ y_2 = & \left[1 + \exp \left(\frac{F_1(V(P), T, y_1, y_2) - F_1(V(P), T, y_1, y_2(1 - n_2))}{N_2 y_2 n_2 kT} - \mu^{gas}(P, T)/kT \right) \right]^{-1} \end{aligned} \quad (12)$$

where y_1, y_2 describes the degree of filling the 1 and 2 types cavities of clathrate hydrate.

3. Computation Details

Considering ice Ih, methane hydrate phases and methane hydrate phases immersed in the ice Ih phase, we used a modified SPCE water–water interaction potential. The parameters describing short-range interaction between the oxygen atoms $\sigma = 3.17 \text{ \AA}$ and the energy parameter $\varepsilon = 0.64977 \text{ kJ mol}^{-1}$ of Lennard-Jones potential of SPCE potential³²⁾ were changed and taken to be $\sigma = 3.1556 \text{ \AA}$; $\varepsilon = 0.65063 \text{ kJ mol}^{-1}$. The charges on hydrogen ($q_H = +0.4238|e|$) and on oxygen ($q_O = -0.8476|e|$) of SPCE model were not changed. The modified SPCE potential significantly improves the agreement between the calculated cell parameters for ice Ih and methane hydrate with the experimental values.

The protons have been placed according to the Bernal–Fowler rule and the water molecules have been oriented so that total dipole moments of the unit cells of ice Ih and hydrates were equal to zero. The long-range electrostatic interactions have been computed by the Ewald method.

3.1 Ice Ih phase

The calculations have been performed on a 64 water molecule supercell of ice Ih. The structure of this model has been obtained by optimizing with a conjugate-gradient

method employing a modified SPCE potential for water. The free energy and the derivatives of free energy have been calculated using $2 \times 2 \times 2$ k-points inside the Brillouin zone.

3.2 Methane xenon hydrate phases

For clathrate hydrate of CS-I, the initial configuration was a single unit cell with 46 water molecules and 8 methane molecules in both large and small cavities. The initial positions of the oxygen atoms and the guests have been taken from the X-ray analysis of ethylene oxide hydrate of CS-I.³²⁾ The orientations of water molecules and the positions of the oxygen atoms and guests have been determined by the conjugate-gradient method at each concerned lattice parameter of the unit cell. The guests are considered as spherically symmetric Lennard–Jones particles. The potential parameters for the methane–methane interaction $\sigma = 3.73 \text{ \AA}$; $\varepsilon = 1.2305 \text{ kJ/mol}$ (OPLS potential) and the potential parameters for the xenon–xenon interaction were $\sigma = 4.047 \text{ \AA}$; $\varepsilon = 1.9205 \text{ kJ/mol}$ and were taken from.³³⁾ The atom–atom interaction potentials for methane–water (xenon–water) interactions were constructed from Lennard–Jones parameters for water and methane (xenon) via the usual combination rules.

3.3 Methane–Ethane hydrate phase

For clathrate hydrate of CS-II, the initial configuration was a single unit cell with 136 water molecules and 16 methane molecules in small cavities and 8 ethane molecules in large cavities. The orientations of water molecules and the positions of the oxygen atoms and guests have been determined by the conjugate-gradient method at each concerned lattice parameter of the unit cell. The potential parameters for the methane–methane interaction are the same: $\sigma = 3.73 \text{ \AA}$; $\varepsilon = 1.2305 \text{ kJ/mol}$ (OPLS potential). For ethane-ethane interactions potential parameters are $\sigma = 4.418 \text{ \AA}$; $\varepsilon = 1.704$ (proposed by Tanaka). In the other case, parameters were taken from OPLS potential, *i.e.* $\sigma = 3.954 \text{ \AA}$; $\varepsilon = 2.01933$. The guest–host interaction potential is also represented in the Lennard–Jones form with relevant parameters estimated from the usual combination rules.

3.4 Methane hydrate phases immersed in the ice Ih phase

The description of thermodynamic properties of hydrate phase immersed in the ice phase was carried out within the framework of macroscopic model.

In the macroscopic model hydrate phase having volume V_{hyd} was located inside ice phase having volume V_{ice} at temperature T_0 and pressure P_0 . For calculation of pressure of hydrate phase immersed in the ice Ih phase, the approximation of the coordinated compression was used, *i.e.* relative change of volume was considered identical to ice and hydrate. Pressure in hydrate at heating ice from T_0 up to some temperature T ice at pressure P_0 was taken from a condition of equality of relative change of equilibrium volume of ice and hydrate:

$$\frac{V_{hyd}(T, P)}{V_{hyd}(T_0, P_0)} = \frac{V_{ice}(T, P_0)}{V_{ice}(T_0, P_0)} \quad (13)$$

The equations of state $V_{ice}(T, P_0)$ and $V_{hyd}(T, P)$ have been calculated using the eq. (4) of the lattice dynamics approach within the quasiharmonic approximation.

4. Results and Discussion

4.1 Phase diagram

The calculated pressure dependence of the chemical potentials of water molecules of Ice Ih, empty host lattice of structure I hydrate, methane (Fig. 1(a)) and xenon (Fig. 1(b)) hydrates of cubic structure I (CS-I) with and without entropy term (last terms of the equations (5), (6)) at temperature $T = 273 \text{ K}$ for methane and Xe hydrates are displayed.

As seen from the Figures changes made to chemical potentials of empty host lattice under influence of guest molecules are significant. There is an increase of difference $\Delta\mu = \mu_{ice} - \mu_Q$ between chemical potentials of ice and host lattice reaching values close to those that are used in construction of phase diagrams within the framework of the van der Waals and Platteeuw theory. Intersection of chemical potential curves of Ice Ih and of the host lattice with the accounting of entropic contribution defines the pressure of monovariant equilibrium at a given temperature.

The calculated pressure dependence of the filling degree of

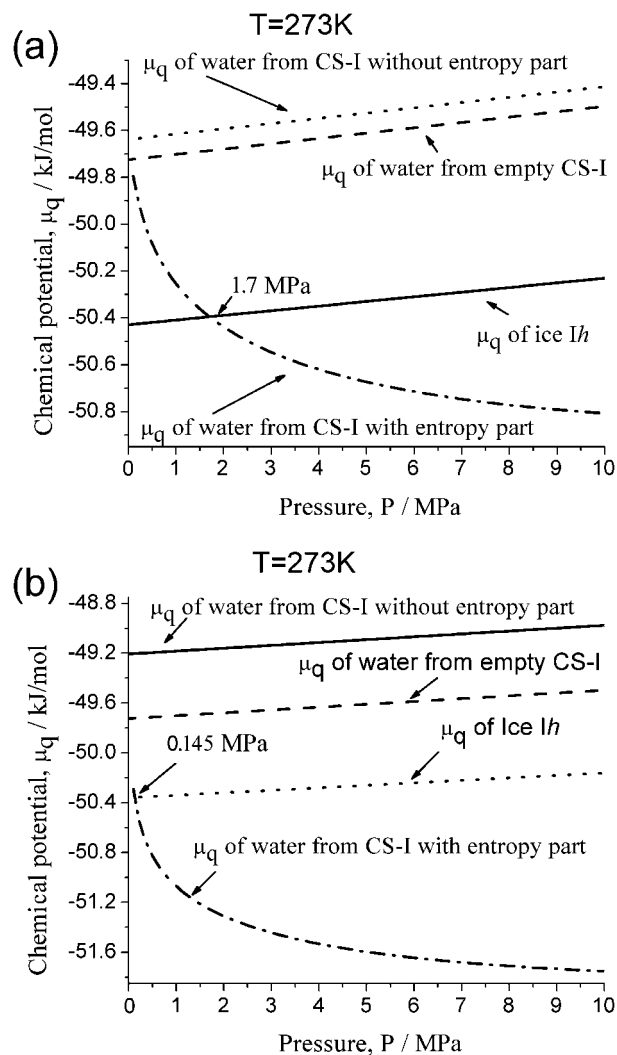


Fig. 1 a) Chemical potentials of water molecules μ_Q of ice Ih, empty host lattice of hydrate of cubic structure I (CS-I), and methane hydrate (CS-I) b) Chemical potentials of water molecules μ_Q of ice Ih, empty host lattice of hydrate of cubic structure I (CS-I), and xenon hydrate.

the small and large cavities of Xe hydrate are shown in Figs. 2. As follows from the results of calculations, filling degrees differ notably from unity at low pressure and approaches closely unit value at pressure increasing already for pressures higher 50 bar for the Xe hydrate of structure I. Analogous calculations for methane hydrate gives results similar to the occupation ratio of Xe hydrate, but the occupation degree of small cages is notable less (Fig. 3). The calculated curves $P(T)$ of monovariant equilibrium of the gas phase, ice Ih, and Xe hydrate are displayed in Fig. 4. The calculated curves for the Xe hydrate agree well with the experiment. The calculated curves $P(T)$ of monovariant equilibrium of the gas phase, ice Ih, and Me hydrate are displayed in Fig. 5. The calculated curves for the Me hydrate agree well with the experiment.

4.2 Hydrate phases immersed in the ice phase

Linked together by hydrogen bonds, the water molecules in clathrate hydrates form the host lattice with the cavities where the guest molecules can be engaged. Properties of clathrate hydrates depend on the structure of the host lattice

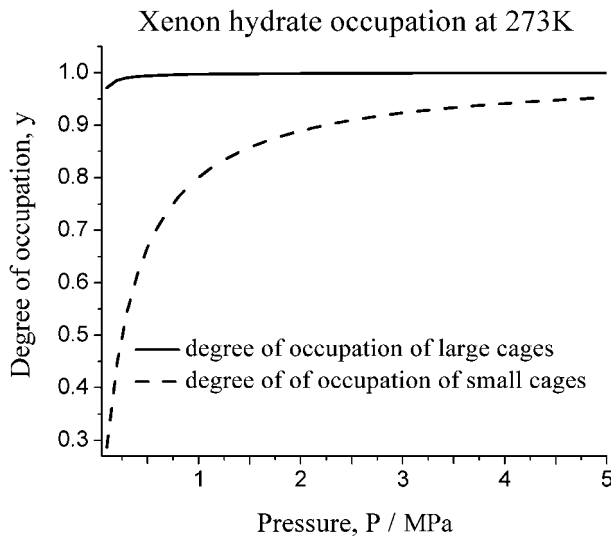


Fig. 2 The degree of filling of the small and large cavities of Xe hydrate CS-I.

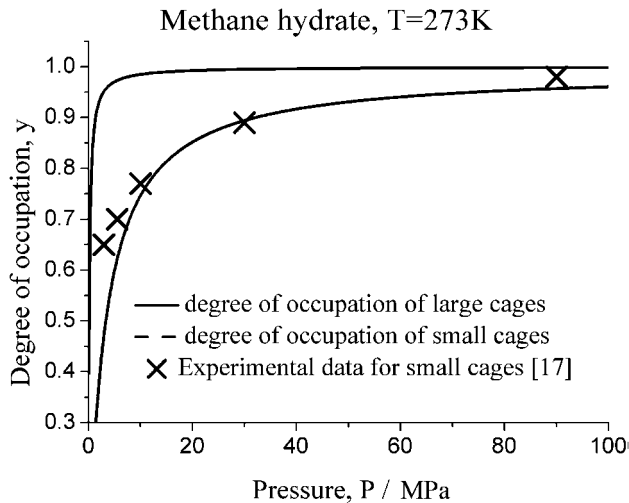


Fig. 3 The degree of filling of the small and large cavities of methane hydrate CS-I. Experimental data was taken from.³⁴⁾

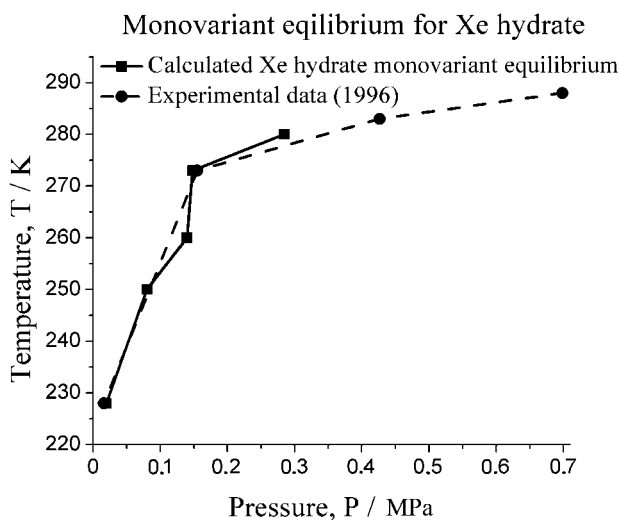


Fig. 4 Calculated and experimental curve $P(T)$ of monovariant equilibrium of the gas phase, ice Ih and Xe hydrate. Experimental data was taken from.³⁵⁾

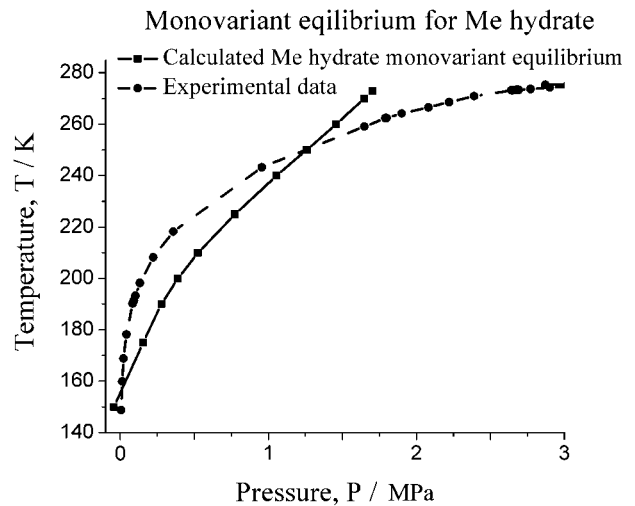


Fig. 5 Calculated and experimental curve $P(T)$ of monovariant equilibrium of the gas phase, ice Ih and Me hydrate. Experimental data was taken from.¹⁾

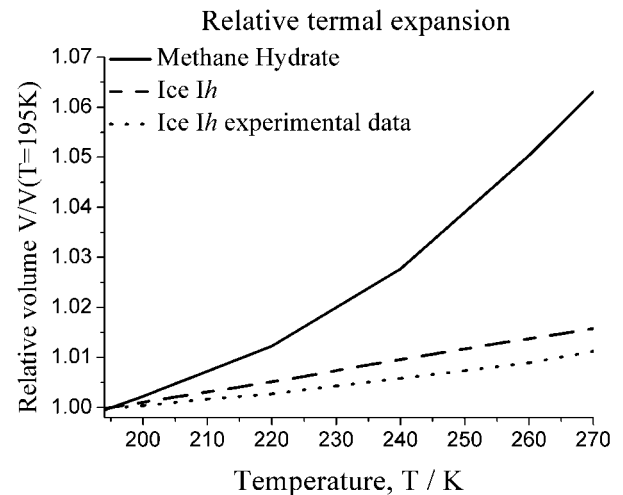


Fig. 6 Relative change of volumes of ice Ih and methane hydrate $V/V(195\text{ K})$. Experimental data for ice Ih was taken from.³⁶⁾

and the kind of guest molecules in these cages. Short-range ordering of the host lattice is similar to that in the hexagonal ice and it may be assumed that properties of the hydrates depending on the short-range ordering of the host lattice are also similar to these in hexagonal ice. However, the thermal expansion of clathrate hydrates is considerably larger than for the hexagonal ice. The guest molecules influence on the host lattice is significant.

The calculated temperature dependences of relative changes of volume $V/V(195\text{ K})$ for Ice Ih and methane hydrate CS-I at pressure $P = 0.1\text{ MPa}$ are displayed in Fig. 6. For Ice Ih the relative change of volume at temperatures from 195 up to 270 K is compared with experimental results.³⁶⁾ It was shown in^{23,24)} for methane hydrate the coincidence of the calculated results and experimental data is sufficiently good at temperatures below 200 K. At higher temperatures than 195 K the methane hydrate exists as a metastable phase, and the calculated relative changes of the volume $V/V(195\text{ K})$

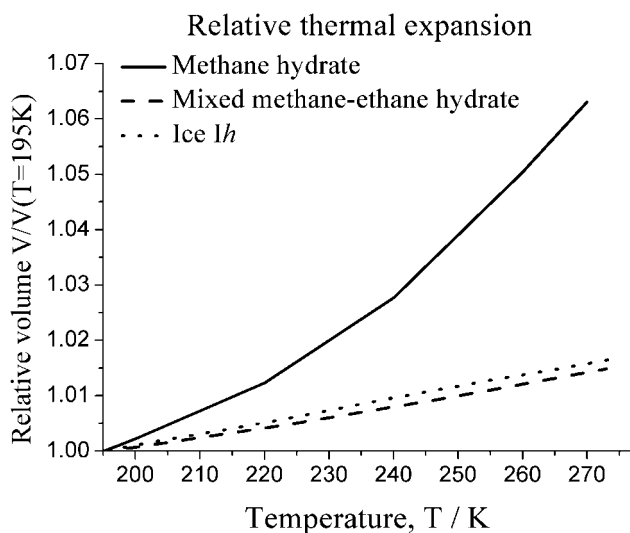


Fig. 7 Relative change of volumes of ice Ih and ethane-methane hydrate $V/V(195\text{ K})$.

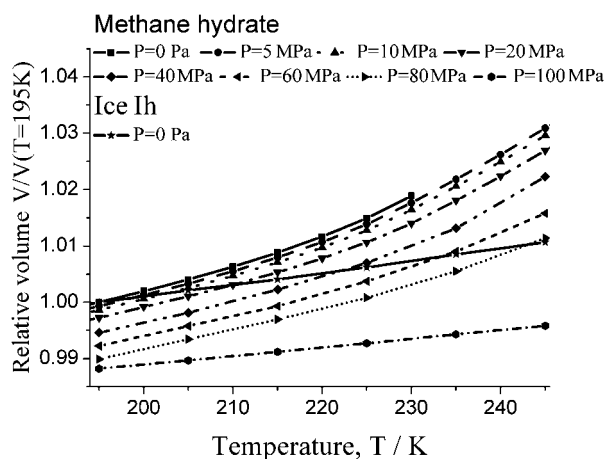


Fig. 8 Calculated thermal expansion of methane hydrate at different values of pressure in comparison with thermal expansion of ice Ih at 0.1 MPa. One unit cell of methane hydrate was taken into account.

become larger than relative changes of the volume $V/V(195\text{ K})$ for Ice Ih.

The calculated temperature dependencies of relative changes of volume $V/V(195\text{ K})$ for Ice Ih and ethane-methane hydrate CS-II at pressure $P = 0.1\text{ MPa}$ are displayed in Fig. 7.

For ethane-methane hydrate CS-II the relative change of volume at temperatures from 195 up to 270 K is compared with experimental results for Ice Ih and the methane hydrate. As can be seen from the relative change of volume of ethane-methane hydrate CS-II coincide with the relative change of volume of Ice Ih at temperatures from 195 up to 225 K and is lower at higher temperature.

In Fig. 8 the temperature dependences of relative volumes $V(P, T = 195\text{ K})/V(P = 0.1\text{ MPa}, T = 195\text{ K})$ for methane hydrate and Ice Ih at different pressure are presented. The temperature dependencies of pressure in hydrate phase immersed in the Ice Ih phase are defined from the crossing of curves of relative volumes for methane hydrate at different pressures and ice Ih as shown in Fig. 8.

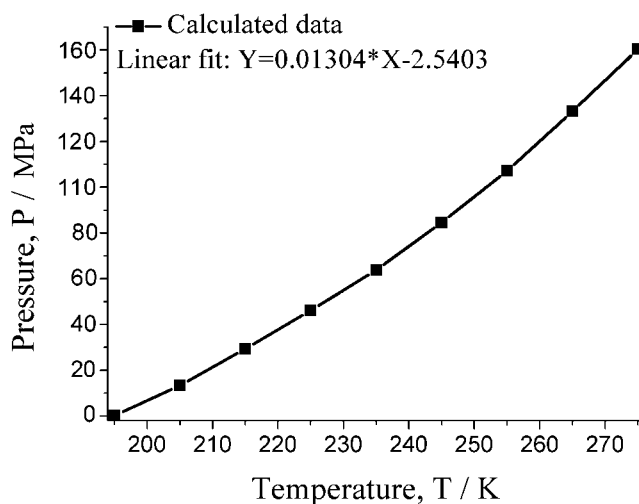


Fig. 9 Calculated dependence of surplus pressure of temperature in methane hydrate cluster included in ice Ih.

The calculated temperature dependence of pressure in hydrate at heating ice from $T = 195\text{ K}$ at pressure $P = 0.1\text{ MPa}$ are displayed in Fig. 9. The calculation shows that with a rise of 1 K in temperature the pressure can be increased up to 1.3–2.0 MPa in the center of cluster of hydrate depending on the temperature. This leads to the situation when the methane hydrate can be thermodynamically stable under heating (overheating of methane hydrate) because it can stay in a region of stability on the methane hydrate phase diagram.

5. Conclusion

The molecular model of inclusion compounds is developed which allow one to calculate thermodynamic functions of inclusion compounds starting from known potentials of intermolecular interactions. In distinction from the well-known theory of van der Waals and Platteeuw the suggested model accounts for the influence of guest molecules on the host lattice and guest-guest interaction. The model is applicable to other inclusion compounds with the same type of composition (clathrate silicon, zeolites, inclusion compounds of semiconductor elements, etc.). On the molecular level the curves of monovariant equilibrium for methane, and Xe hydrates in a wide range of pressure and temperature have been determined. The calculated curves of monovariant equilibrium agree well with experiment.

Increasing of pressure occurs inside methane hydrate phases immersed in the ice phase under increasing temperature, and if the ice structure does not become destroyed, the methane hydrate will have larger pressure than ice phase. The methane hydrate remains thermodynamically stable under heating (overheating of methane hydrate). This is because of the thermal expansion of methane hydrate in a few times larger than ice one. Thermal expansion of hydrate went up by thermal expansion of ice because it can be stay in a region of stability on methane hydrate phase diagram. The utter lack of preservation behavior in CS-II methane-ethane hydrate can be explained by the fact that the thermal expansion of ethane-methane hydrate coincide with than ice one it do not pent up by thermal expansion of ice.

Acknowledgments

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