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Influence of Nitrogen on Structure, Guest Distribution and Hydrate Formation Conditions of the Mixed CO2–CH4 and CO2–CH4–N2 Gas Hydrates

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Abstract: In this contribution, a method based on a solid solution theory of clathrate hydrate for multiple cage occupancy, host lattice relaxation and guest-guest interactions has been presented to estimate hydrate formation conditions of binary and ternary gas mixtures. We have performed molecular modeling of structure, guest distribution, and hydrate formation conditions for the CO_2 + CH_4, and CO_2 + CH_4 + N_2 gas hydrates. In all considered systems with and without N2, at high and medium content of CO_2 in the gas phase we have found that CO_2 is more favorable to occupy clathrate hydrate cavities than CH_4 or N_2. Addition of N_2 to the gas phase increases ratio concentration CO_2 in compressing with concentration CH_4 in clathrate hydrates and makes gas replacement more effective. The mole fractions of CO_2 in CO_2 + CH_4 + N_2 gas hydrate rapidly increases with the growth of its content in the gas phase. And the formation pressure of CO_2 + CH_4 + N_2 gas hydrate rises in comparison with the formation pressure of CO2 + CH4 gas hydrate. Obtained results agree with the known experimental data for simple CH4, CO2 gas hydrates and mixed CO2 + CH4 gas hydrate.

Keywords: gas separation; lattice dynamic; mixed gas hydrates, greenhouse gases, computer modeling

1. Introduction

Due to concerns of increasing of global warming effect, the capture from industrial flue gas and long-term storage of carbon dioxide are among the most important challenges facing the world scientific community today.

Various strategies [1] to sequester carbon dioxide have been proposed but the technology to safely storage CO2 in massive quantities has not been fully developed.

Currently, the leading approach to this problem involves injecting CO2 into spent natural gas reservoirs deep underground [2]. In seismically active zones such as Japan, use of this method of CO2 storage may be lead to gas leakage due to geological perturbations such as earthquakes or fractures. Another approach, offered by Ohgaki and Inoue [3], is the sequestration of CO2 as solid hydrates by formation of CO2 clathrate hydrate. Recently, the injection of CO2 in porous sediments at a depth of several hundred meters below the deep ocean floor has been proposed as an alternative long term sequestration option that would be resistant to geophysical perturbations [4]. Such deposition of CO2 prevents the transport of the CO2 back to the surface due to the formation of CO2 clathrate hydrate capping layer that reduces the migration. The authors estimate this storage strategy could remain intact for millions of years. It has also been shown that CO2 hydrates have anomalously low dissociation rate at atmospheric pressure. This self-preservation effect takes place

in the temperature range 245-271 K that could be significant in practice for the CO_2 storage in the form of clathrate hydrates [5]. Clathrate hydrates are non-stoichiometric inclusion compounds consisting of water (*host*) molecules forming crystalline framework in which cavities (cages) there can be included guest molecules. There exist mainly three types of gas hydrates in Nature: hydrates of cubic structure CS-I, cubic structure CS-II, and hexagonal structure HS-III [6]. The structure of formed hydrate is determined primarily by the size of guest molecules. So, large guest molecules such as propane and isobutane as well as small guests, in particular, oxygen, nitrogen and hydrogen, form the cubic structure CS-II. Guest molecules of intermediate size such as methane, xenon and carbon dioxide form hydrates of the cubic structure CS-I. There are necessary the presence simultaneously of two types of guest molecules to form the hexagonal structure HS-III: very large molecules, e.g., 2, 2-dimethylbutane, and small molecules, for example, methane. The hydrate structures differ by sizes and numbers of cavities in their unit cells. Large amounts of natural gas composed of mainly methane and other hydrocarbons in the form of solid hydrates are stored on continental margins and in permafrost regions [6]. Technology of simultaneous production of hydrocarbon raw and greenhouse-gas sequestration can be promising. Carbon dioxide sequestration in deep-sea sediments or permafrost regions can be performed simultaneously with natural gas recovery by swapping hydrocarbon molecules in the hydrate cages for carbon dioxide molecules, thus providing a mechanism of hydrocarbons production and greenhouse-gas sequestration [7-9]. The replacement of CH_4 hydrates by CO_2 hydrates has been studied [7] for recovering CH_4 gas. When mixture of water with gas or liquid CO_2 itself is put under certain pressure, a solid CO_2 hydrate can be formed at much milder P-T-conditions than CH_4 hydrate [10]. Thus, the swapping process between two gaseous guests is considered to be a promising approach to long-term storage of CO_2. When the CH_4 hydrate is put under certain pressure [8, 9] of CO_2 / N_2 gas mixture, a decomposition of CH_4 hydrates and a solid mixed hydrate containing CO_2 can appear with recovering CH_4 gas. The direct use of a (CO_2 + N_2) gas mixture (20 mole% CO_2 and 80 mole% N_2 to reproduce flue gas from a power plant) instead of pure CO_2 greatly enhances the overall CH_4 recovery rate in complex marine systems and reduces costs [11] of CO_2 separation from flue gas. Great number of experimental and theoretical studies concerning stability and composition of gas hydrates formed from gas mixtures has been published in last decade [6, 12-22]. In particular, comparison of numerous experimental data on phase equilibria in systems *water–mixture of methane and carbon dioxide, water–mixture of nitrogen and carbon dioxide* were presented in papers [23-28]. The stability of CO_2 / N_2 or CO_2 / CH_4 mixed hydrates were studied in various conditions and it was shown that the three-phase *hydrate–water–vapor* equilibrium curves were shifted to higher pressures at all considered temperature with decrease [25-28] of CO_2 concentration in the vapor phase. The statistical thermodynamic theory of *Van der Waals and Platteeuw* [29] is used for modeling the hydrate phase contain nitrogen [23-25]. The main assumptions were made in the original *VdW&P* model, it states that each cavity can contain at most one gas molecule. However, *Kuhs and co-workers* [30,31] found the first direct evidence for multiple occupancy of the cages in nitrogen hydrate. These results have been confirmed by molecular dynamics simulations of CS-II nitrogen hydrate with varying cage occupancies and at different conditions [32-33]. For the more correct prediction of hydrate phase equilibria, it is necessary to consider possibility of multiple occupancy of the cages in the gas hydrate containing nitrogen.

The aim of this paper is investigation of possibility to recovery of methane from methane hydrates using either CO_2 or a CO_2 / N_2 gas mixture the hydrate phase were treated with the solid solution theory of clathrate hydrate for multiple cage occupancy, host lattice relaxation and guest-guest interactions [34-38]. With this goal there have been determined the dependencies of the compositions of the gas hydrates formed from methane + carbon dioxide, nitrogen + carbon dioxide binary gas mixtures and methane + carbon dioxide + nitrogen ternary gas mixtures as well as of the formation conditions of these hydrates in dependence on temperature and pressure for different compositions of the gas phase.

2. Methods

2.1. Implemented Theoretical Models

In order to estimate accurately the thermodynamic properties of clathrate hydrates, we developed an approach based on the solid solution theory of clathrate hydrate for multiple cage occupancy, host lattice relaxation and guest-guest interactions [34-38]. The method based on only one from several assumptions of the original *VdW&P* theory [29]: free energy of clathrate hydrate does not depend on the arrangement of guest molecules in cavities at fixed values of filling degrees for each definite type of cavities. In this approach the lattice dynamics method that takes quantum effects into account is used and the crystalline host lattice is considered as non-rigid, able to change volume depending on the type of the guest molecules and permits to describe first-order phase transitions.

The mathematical formalism of the present model for the general case and in the case of clathrate hydrates with two types of cavities and one type of guest was described in our previous studies [34,35]. In contrast to our previous work in present work, we have formulated our approach for the hydrate having two types of cavities, large (*L*) and small (*S*), and the possibility of single occupancy of small and large cavities by *a*, *b* and *c* type guests and single occupancy large cavities by *a b* type guests and multiple occupancy of large cavities by *c* type guests.

In the mentioned approximation, free energy of the clathrate hydrates can be presented as:

$$F = F_1(V,T,\{y\}) + k_B T \sum_{t,l,i_l} N_t \left[\left(1 - \sum_{t,l,i_l} y_t^{i_l l}\right)\ln\left(1 - \sum_{t,l,i_l} y_t^{i_l l}\right) + \frac{y_t^{i_l l}}{i_l!}\ln y_t^{i_l l} \right], \tag{1}$$

where: a) for binary clathrate hydrates with cavities of two types including two types of guest molecules and the possibility of single occupancy for type *a* guests and single occupancy for type *b* guests of both the small and large cavities: $i_l = 1$, $l = a,b$, $t = S,L$; F_1 is the part of free energy at a given degree of filling of the guest molecules in the *S* and *L* cavities: $\{y\} = \{y_S^a, y_L^a, y_S^b, y_L^b\}$, $y_t^l = N_t^l/N_t$ are filling degrees for cavities of *t* -th type ($t = S,L$) by guest molecules of *l* -th type ($l = a,b$); N_t is the number of cavities of *t* -th type; N_t^l is the number of guest molecules of *l* -th type contained in cavities of *t* -th type;

b) for ternary clathrate hydrates with cavities of two types including three types of guest molecules and the possibility of single occupancy for type *a* guests and single occupancy for type *b* guests of both the small and large cavities and the possibility of single occupancy for type *c* guests the small and multiple occupancy large cavities $l = a,b,c$, $i_a = 1$, $i_b = 1$, $i_c = 1,2$, $t = S,L$; F_1 is the part of free energy at a given degree of filling of the guest molecules in the *S* and *L* cavities: $\{y\} = \{y_S^a, y_L^a, y_S^b, y_L^b, y_S^c, y_L^c, y_L^{2c}\}$, $y_t^{i_l l} = N_t^{i_l l}/N_t$ is filling degree for cavity of *t* -th type ($t = S,L$) by guest molecules of *l*-th type ($l = a,b,c$); N_t is number of cavity of *t* -th type; $N_t^{i_l l}$ is the number of guest molecules of *l* -th type contained in cavities of *t* -th type.

In our cases for the binary clathrate hydrates $i_l = 1$, $l = CO_2, CH_4$, $t = S,L$ and for the ternary clathrate hydrates $i_{CO_2} = 1$, $i_{CH_4} = 1$, $i_{N_2} = 1,2$, $l = CO_2, CH_4, N_2$, $t = S,L$. In the models it is considered that that molecules of CO_2, CH_4, N_2 can single occupy both the small and large cavities, while molecules of N_2 can also double occupy both the large cavities.

For a given arrangement $\{y\}$ of the guest molecules in the cavities the free energy $F_1(V,T,\{y\})$ of the crystal can be calculated within the framework of a lattice dynamics approach as

$$F_1(V,T,\{y\}) = U + F_{\text{vib}}, \tag{2}$$

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

$$F_{\text{vib}} = \tfrac{1}{2}\sum_{j\vec{q}} \hbar\omega_j(\vec{q}) + k_B T \sum_{j\vec{q}} \ln\left(1 - \exp(-\hbar\omega_j(\vec{q})/k_B T)\right), \tag{3}$$

where $\omega_j(\vec{q})$ is the j-th eigenfrequency of crystal vibration and $\vec{q}$ is the wave vector. Free energy is computed for several values of volume, it has a minimum corresponding to the equilibrium structure at zero pressure.

The equation of state is found by numerical differentiation of the free energy with respect to volume

$$P(V,T) = -\left(\frac{\partial F(V,T,\{y\})}{\partial V}\right)_0. \tag{4}$$

Then one finds chemical potentials $\mu_t^{i_l l}$ of guest molecules in the hydrate by numerical differentiation of the free energy with respect to the number of guest molecules.

$$\mu_t^{i_l l}(P,T,\{y\}) = \left(\frac{\partial F(V,T,\{y\})}{\partial N_t^{i_l l}}\right)_0 = \mathring{\mu}_t^{i_l l} + \text{kT}\ln\frac{y_t^{i_l l}}{i_l!\left(1-\sum_{t,l,i} y_t^{i_l l}\right)}, \tag{5}$$

$$\mathring{\mu}_t^{i_l l} = \left(\frac{\partial F_1(V(P),T,\{y\})}{\partial N_t^{i_l l}}\right)_0. \tag{6}$$

If the free energy F is known then the Gibbs free energy

$$\Phi(P,T,\{y\}) = N_Q \mu_Q(P,T,\{y\}) + \sum_{t,l,i} N_t^{i_l l}\mu_t^{i_l l}(P,T,\{y\}) = F(V(P),T,\{y\}) + PV(P). \tag{7}$$

Expressed in terms of the chemical potentials of the host and guest molecules can be found:

$$\mu_Q(P,T,\{y\}) = \mathring{\mu}_Q(\{y\}) + \text{kT}\sum_{t,l,i_l} \nu_t\left(1 - \sum_{t,l,i_l} y_t^{i_l l}\right), \tag{8}$$

$$\mathring{\mu}_Q(P,T,\{y\}) = \frac{1}{N_Q} F_1(V(P),T,\{y\}) + \frac{1}{N_Q} PV(P) - \sum_{t,l,i_l} \nu_t y_t^{i_l l} \mathring{\mu}_t^{i_l l}(P,T,\{y\}), \tag{9}$$

where $\nu_t = \frac{N_t}{N_Q}$, N_Q is the number of water molecules.

P-T line of monovariant equilibrium of different hydrates and ices can be found from the equality condition of the chemical potentials of water molecules in hydrates and in ice or in liquid phase:

$$\mu_Q(P,T,\{y\}) = \mu_Q^{\text{ice}}(P,T); \mu_Q(P,T,\{y\}) = \mu_{\text{wA}_g}(P,T). \tag{10}$$

Analogously equality of chemical potentials of guest molecules in hydrate and in the gas phase can be written as:

$$\mu_t^{i_l l}(P,T,\{y\}) = \mu_{i_l l}^{\text{g}}(P,T). \tag{11}$$

The chemical potential of guest molecules in the gas phase were calculated using the following equations for a non-ideal gas mixture with the *Lennard-Jones* interaction between molecules [20]:

$$\mu_i^{\text{g}}(V,T) = k_B T \ln\left[\frac{N_i^g}{V}\left(\frac{2\pi\hbar^2}{m_i T}\right)^{3/2}\right] - \frac{\partial}{\partial N_i^g}\left(Nk_B T\ln\left(1 - N\frac{\sum_{i,j}\varepsilon_{ij}x_i^g x_j^g}{V}\right) - N^2\frac{\sum_{i,j}\sigma_{ij}x_i^g x_j^g}{V}\right), \tag{12}$$

were ε_i, σ_i are Lennard–Jones parameters. Interaction parameters between molecules of different types are defined by the combination rules: $\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$ and $\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}$; $x_i = N_i^g / N^g$ is the mole fraction of the i-th component in the gas mixture; N^g is the number of guest molecules in gas phase; N_i^g is the number of guest molecules of l-th type in gas phase; m_i is the molar mass of the i-th component. The first term in the Equation (12) corresponds to the chemical potential of the ideal gas and the second two corrections appearing for real gases.

The chemical potential of liquid water, μ_{wA_q} was taken from the model proposed earlier [39] and is given by

$$\mu_{\mathrm{wA}_q}(P,T) = \frac{T}{T_0} g_{w_0 L_{\mathrm{pre}}} - \int_{T_0}^{T} \frac{dT'}{T} h_{\mathrm{wL_{Pure}}} + \int_{P_0}^{P} v_{\mathrm{wL_{Pure}}} \, dP', \tag{13}$$

where T_0 is the initial temperature and P_0 is the initial pressure. The following constants were also used defined in [39]: the Gibbs energy of formation $g_{w_0 L_{\mathrm{pre}}}$, the molar enthalpy of water $h_{\mathrm{wL_{Pure}}}$, and the water volume $v_{\mathrm{wL_{Pure}}}$, these constants refer to pure water. Instead of using, the empirical value of $g_{w_0 L_{\mathrm{pre}}}$ we calculated this parameter directly by using the lattice dynamic method. This parameter can be evaluated from the chemical potential of water, μ_{wA_q}, which should be equal to μ_0^{ice} of hexagonal ice calculated at the ice I_h melting point at standard pressure and temperature. The degrees of cage filling have been found from formulae (5), (11):

$$y_t^{i_l l} = \frac{\beta_t^{i_l l}}{1 + \beta_t^{i_l l}}; \beta_t^{i_l l} = \exp\{\frac{1}{\mathrm{kT}}\left[\mu_l^{\mathrm{gas}} - \mu_t^{i_l l}\right]\}. \tag{14}$$

For quantitative determination of the hydrate composition as a function of the gas phase composition the following relations for fractions of the filled large ($C_L^{i_l l}$) and small ($C_S^{i_l l}$) cages have been used, and mole fractions in guest subsystems of l type guest molecules included in hydrate phase (x_l^h) have been used:

$$C_t^{i_l l} = \frac{y_t^{i_l l} N_t}{\sum_{t,l,i_l} y_t^{i_l l} N_t}; x_l^h = \sum_{i_l,t} C_t^{i_l l}. \tag{15}$$

2.2 Simulations Details

The unit cells were chosen as the simulation cell of CS-I (46 water molecules forming 6 large and 2 small cages) and CS-II hydrates (136 water molecules forming 8 large and 16 small cages). Large cages as well as small ones can be filled by one carbon dioxide or methane molecule. Possibility of double filling of large or small cages by these guest molecules was not considered due to comparatively large size of these molecules. For modeling of ice I_h the simulation supercell containing 32 unit cells, i.e. 128 water molecules, was used. Coulomb interactions have been calculated by the *Ewald* method. The protons were placed according to the *Bernal-Fowler* rules [40] and the water molecules were oriented such that the total dipole moments of the simulation cells of ice and the hydrates were zero with a precision of better than 0.1% of the magnitude of the dipole moment of a single water molecule. The interaction of *water-water* molecules in hydrates and in ice have been described by the modified SPC/E potential [41]:

$$U_{\mathrm{ij}}(r) = 4\varepsilon_{\mathrm{ij}}\left[\left(\frac{\sigma_{\mathrm{ij}}}{r}\right)^{12} - \left(\frac{\sigma_{\mathrm{ij}}}{r}\right)^{6}\right] + \frac{q_i q_j}{r}, \tag{16}$$

with the *Lennard-Jones* parameters $\sigma_O = 3.1556$ Å, $\varepsilon_O = 0.65063$ kJ/mole. Charges on hydrogen atoms were $q_H = +0.4238|e|$ and on oxygen atoms $q_O = -0.8476|e|$. This parameters selection had allowed to reach good agreement with experimental data [34,35]. For description of interactions of guest molecules between each other and with water molecules the *Lennard-Jones* potential was used with the parameters $\sigma = 3.73$ Å, $\varepsilon = 1.2305$ kJ/mole for methane molecules [42], $\sigma = 4.00$ Å, $\varepsilon = 1.5801(1)$ kJ/mole for carbon dioxide molecules [43], and $\sigma = 3.6154$ Å, $\varepsilon = 0.844$ kJ/mole for nitrogen molecules [44].

3. Results and Discussion

A. Phase Equilibria Gas–Hydrate

The divariant equilibria *gas–hydrate* are described by the Equation (11). This equation represents the conditions of equality of chemical potentials of guest molecules in hydrate with the gas phase of the same kind of molecules in dependence on pressure and temperature. The comparison of degrees of filing for binary mixed hydrate (50% CH_4 and 50% CO_2 in gas phase) and ternary (15% CH_4 and 15% CO_2 and 70% N_2 in gas phase) at the temperature T = 277 K are presented at

Figure 1a, b. One can see (Figure 1a) that carbon dioxide molecules occupy both small and large cavities more preferably than methane. The difference in degrees of filling is the result of slightly larger size of CO_2 molecules and there more strong interaction with water molecules. After addition of nitrogen to the gas phase, the tendency is the same (Figure1b) but in this case, cavities occupation by N_2 molecules can be concurred by CO_2 and CH_4 molecules. In spite of more than two-times higher concentration of nitrogen in the gas phase, methane and carbon dioxide molecules more rapidly occupy the large cavities; so, at the pressure 10 MPa only 19% of large cavities are filled by N_2 whereas 24% and 57% are filled by CH_4 and CO_2, respectively. Other situation is observed for small cavities filling. In this case, N_2 molecules become preferable and can concur with larger molecules of CH_4 and CO_2. Therefore, at the same pressure 10 MPa the cages are filled by N_2, CH_4 and CO_2 in amounts 37%, 19% and 31%, respectively. There is also the tendency of growth in cage filling by nitrogen molecules with the pressure increase. In both binary and ternary hydrates, one can see the noticeable growth of ratios $\frac{y_L^{CO_2}}{y_L^{CH_4}}$ and $\frac{y_S^{CO_2}}{y_S^{CH_4}}$ with the nitrogen addition. For binary CO_2 + CH_4 hydrate $\frac{y_L^{CO_2}}{y_L^{CH_4}} = 2.09$ while for ternary CO_2 + CH_4 + N_2 hydrate $\frac{y_L^{CO_2}}{y_L^{CH_4}} = 2.38$. At the same time, for binary CO_2 + CH_4 hydrate $\frac{y_S^{CO_2}}{y_S^{CH_4}} = 1.38$ and for ternary CO_2 + CH_4 + N_2 hydrate $\frac{y_S^{CO_2}}{y_S^{CH_4}} = 1.63$. This means that with addition of N_2 to the gas phase nitrogen molecules more readily displace CH_4 then CO_2 molecules.

(a)   (b)
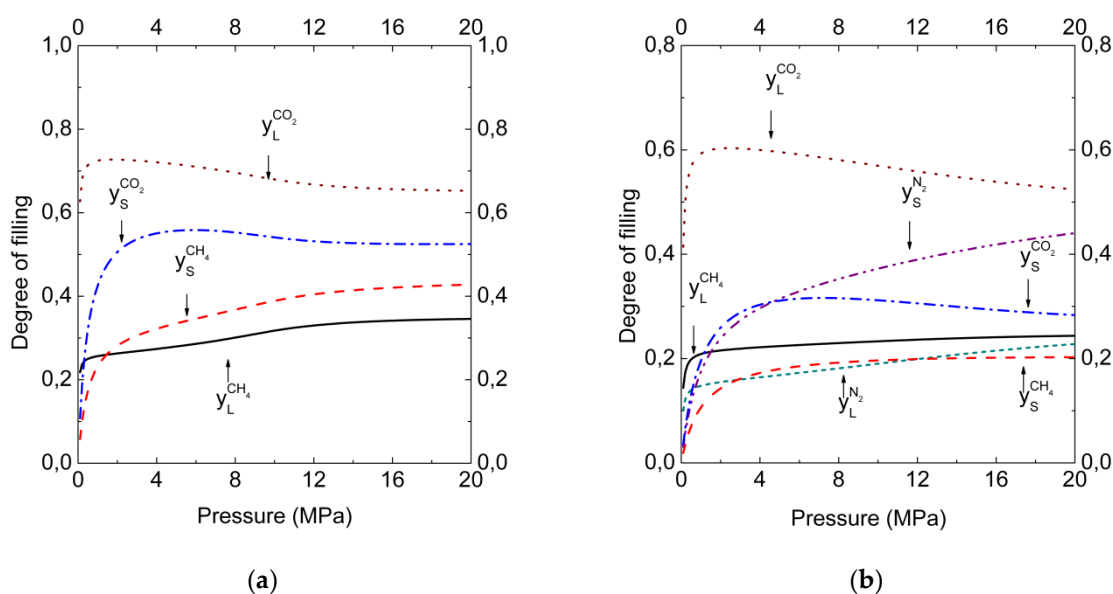
Figure 1. Degree of cage filling for large and small cavities in hydrate at equilibrium conditions at T = 277 K. Gas phase mole fractions are: (a) binary mixture containing carbon dioxide (50%) and methane (50%); (b) ternary mixture containing carbon dioxide (15%), methane (15%), and nitrogen (70%) ($y_L^{CH_4}$- solid; $y_S^{CH_4}$ - dashed; $y_L^{CO_2}$ - dotted; $y_S^{CO_2}$ - dash-dotted; $y_S^{N_2}$ - dash-dot-dotted; and $y_L^{N_2}$ - short dashed lines). The total number of calculated points is equal to 200 with a pressure step of 0.1 MPa for each curve.
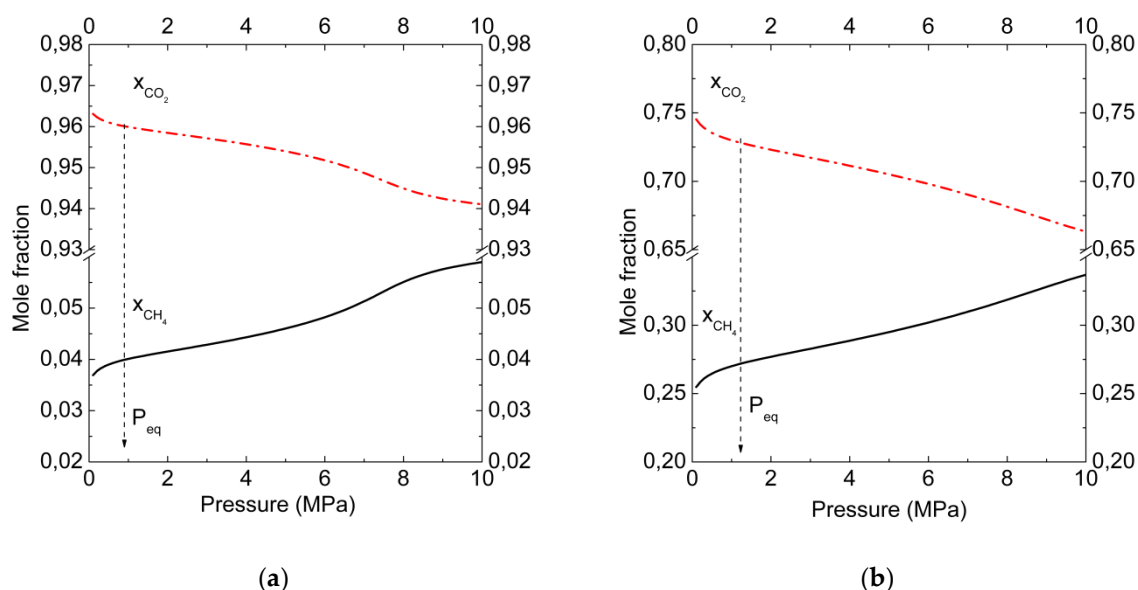
Figure 2. Mole fraction of carbon dioxide and methane in binary hydrates at T = 273 K. Gas phase consists of: (a) carbon dioxide (90%) and methane (10%); (b) carbon dioxide (50%) and methane (50%) (x_{CH_4} - solid; and x_{CO_2} - dash-dotted lines). The total number of calculated points is equal to 100 with a pressure step of 0.1 MPa for each curve.

Figure 2a, b shows the change of CO_2 and CH_4 mole fractions in binary hydrates in dependence on pressure for two gas phase compositions at T = 273 K. Analogous data of mole fractions change for, CO_2, CH_4 and N_2 in ternary hydrates at T = 273 K are presented on Figure 3. The arrows show the equilibrium formation points for hydrates. The intriguing result is that with growth of pressure the CO_2 fraction in hydrate decreases while CH_4 fraction grows. It correlates with results for filling of large and small cavities (Figure 1a).
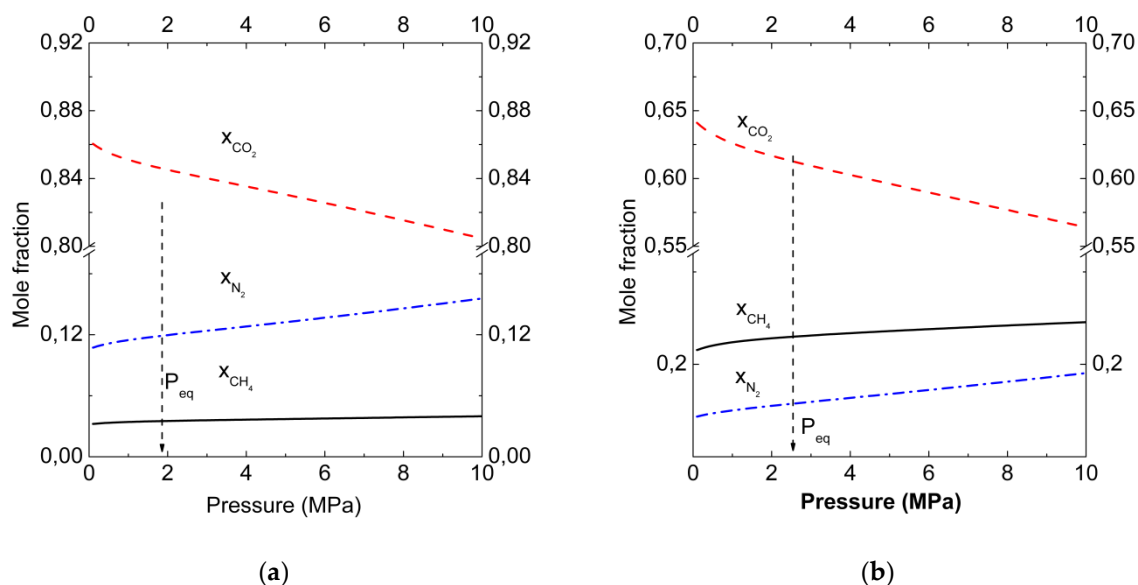
Figure 3. Mole fraction of carbon dioxide, methane and nitrogen in ternary hydrate phases at T = 273 K. Gas phase consists of: (a) carbon dioxide (27%) and methane (3%) with nitrogen (70%); (b) carbon dioxide (15%), methane (15%) and nitrogen (70%) (x_{CH_4} - solid; x_{CO_2} - dashed; and x_{N_2} - dash-dotted lines). The total number of calculated points is equal to 100 with a pressure step of 0.1 MPa for each curve.

Another interesting finding is that the rate of CO_2 fraction decrease in hydrate phase is small for high CO_2 concentration in gas phase (Figure 2a) and it increases with CO_2 concentration decrees. At temperature T = 273 K (Figure 2a, b) in the pressure interval 1 to 10 MPa for the gas mixture 90% CO_2 and 10% CH_4 the change of x_{CH_4} or x_{CO_2} is about 0.022 while for gas mixture 50% CO_2 + 50% CH_4 it becomes about 0.082 that is almost four times larger.

After addition of nitrogen to binary carbon dioxide + methane mixture (Figure 3), the amount of these gases stored in hydrate phase decrease but not drastically. At the formation pressure (1.8 MPa at T = 273 K) for the ternary gas mixture 27% CO_2 + 3% CH_4 + 70% N_2, (Figure 3a) the relative fraction of CO_2 in hydrate was found to be 0.847 instead of 0.96 for binary mixture 90% CO_2 + 10% CH_4. One can see that a large excess of nitrogen at this conditions is weak and its relative fraction in hydrate was found to be 0.118. Methane, with its low content in gas phase (3%) has fractional content is 0.035. In comparison to hydrate phase formed from ternary gas mixture 15% CO_2 + 15% CH_4 + **70**% N_2 (Figure 3b), the situation has changed notably. First, now methane occupies notable part of hydrate cavities and mole fraction of methane reaches 0.229 at the formation pressure. Nitrogen content in hydrate became 0.163 that is almost 40% higher than in the previous case. Methane and nitrogen can replace carbon dioxide in cavities but CO_2 molecules still occupy more than 60% of cavities (mole fraction is 0.614). The increase of relative gas fraction content in hydrates with pressure is almost equal for different gas phase compositions (0.06 for 27% CO_2 and 0.08 for 15% CO_2 in gas mixtures, respectively).

In all considered systems with and without N_2, at high and medium content of CO_2 in the gas phase we have found that CO_2 is more favorable to occupy clathrate hydrate cavities than CH_4 or N_2. Moreover, addition of N_2 to the gas phase increases ratio $\frac{x_{CO_2}}{x_{CH_4}}$. For mixtures 50% CO_2 + 50% CH_4 and 15% CO_2 + 15% CH_4 + 70% N_2 this ratio increased by 1.5% and for mixtures 90% CO_2 + 10% CH_4, and 27% CO_2 + 3% CH_4 + 70% N_2 by about 1%. Therefore, addition of N_2 makes gas replacement more effective.

B. Phase Equilibria Gas–Hydrate–Ice (Water)

Calculation of P, T-diagrams for phase equilibria *gas–hydrate–ice (water)* described by the Equations (10) , (11) carried out earlier for one-component hydrates of methane, and reproduced the experimental data with good accuracy [45,46].
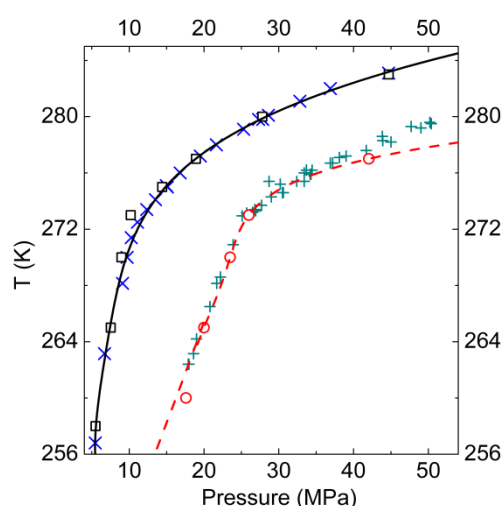
Figure 4. *P, T*-diagram of phase equilibria *gas–hydrate–ice (water)* for one-component hydrates of carbon dioxide and methane. The results of calculations for carbon dioxide are presented by open square, experimental data [6] by skew crosses. For methane calculated data are shown by open circles and experimental data [6] by crosses.

The modeling was performed in the framework of the molecular model described above hear such calculations were conducted for carbon dioxide hydrates. The resulting curves of phase equilibria also are in reasonable agreement with experimental data. In Figure 4 there are presented the calculated curves of phase equilibria *ice–gas–hydrate* for the considered one-component hydrates of carbon dioxide and methane as well as the available experimental data [6] for comparison.

The calculation of hydrate formation pressures as well as of CO_2 fraction in hydrate in dependence on gas phase composition were performed for binary $CO_2 + CH_4$ mixtures at temperatures 273 K and 277 K (Figure5 a,b). The temperatures were chosen in order to describe gas equilibria for both *gas–hydrate–ice* and *gas–hydrate–water*.

(a)   (b)
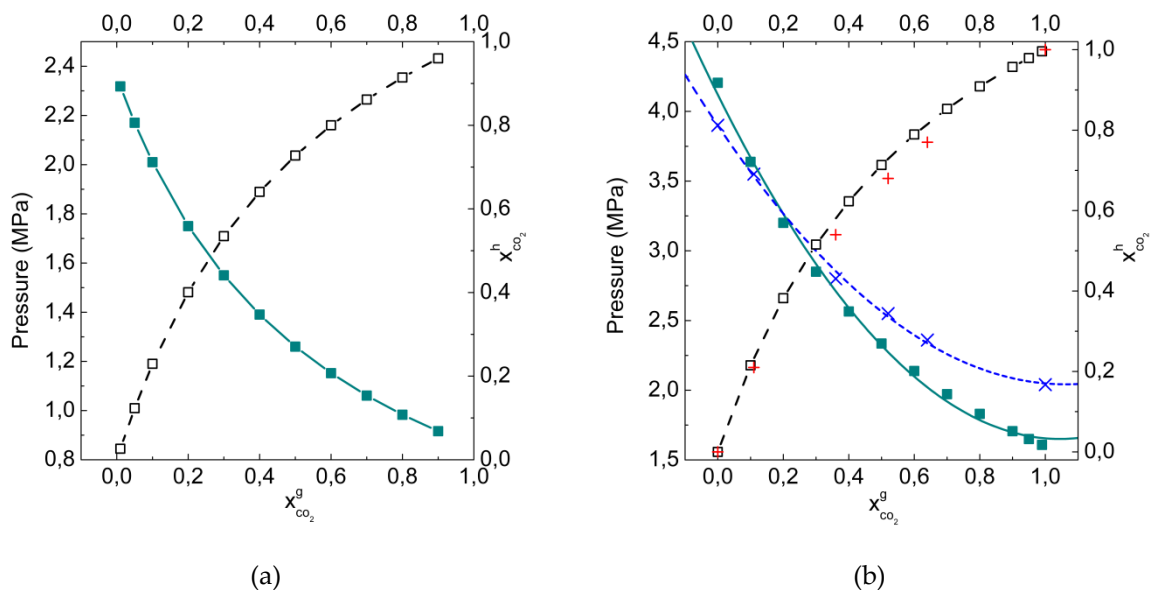
Figure 5. P–x diagram of the binary hydrates of methane and carbon dioxide at T=273 K (a) and T=277 K (b), skew crosses - experimental data [47] of mole fraction carbon dioxide in hydrate phase, crosses - experimental data [47].

It is notable that carbon dioxide fills cages more actively than methane. For example, at temperature 273 K, the hydrate formation pressure and equimolar composition of the gas phase (50% methane, 50% carbon dioxide), fraction of CO_2 molecules in hydrate reaches 73% and fraction of CH_4 about 27%. At temperature, 277 K fractions of gas molecules in hydrate are 70% and 30%, respectively. I.e., the ratio of occupancies by CO_2 and CH_4 is 2.7:1 for 273 K and 2.3:1 for 277 K. These results of calculations agree well with experimental data [47]. It has to be noted that with increase of temperature the fraction of CO_2 in hydrate decreases. That can be connected with the increase of pressure, which is necessary for gas hydrate formation. In this case, the methane molecules can concur with carbon dioxide molecules to occupy mainly small hydrate cavities. It is

Table 1. *P-T-x* equilibria *ice (water)-gas-hydrate* systems for $CO_2 + CH_4$ gas mixture.

$x_{CO_2}^g$ [a]	P_{eq}^{258} [b] (MPa)	$x_{CO_2}^h$ [c]	P_{eq}^{273} [d] (MPa)	$x_{CO_2}^h$ [e]	P_{eq}^{277} [f] (MPa)	$x_{CO_2}^h$ [g]	S_t [h]
1.00	0.55	1.00	1.02	1.00	1.90	1.00	CS-I
0.70	0.69	0.88	1.06	0.86	2.27	0.84	CS-I
0.50	0.83	0.76	1.26	0.73	2.62	0.70	CS-I
0.30	1.03	0.58	1.55	0.54	3.09	0.50	CS-I
0.00	1.66	0.00	2.40	0.00	4.20	0.00	CS-I

[a] $x_{CO_2}^g$ is a mole fraction CO_2 in gas phase;

[b] P_{eq}^{258} is an equilibria pressure at T=258 K;

[c] $x_{CO_2}^h$ is a mole fraction CO_2 in hydrate phase;

d P_{eq}^{273} is an equilibria pressure at T=273 K;

e $x_{CO_2}^h$ is a mole fraction CO_2 in hydrate phase;

f P_{eq}^{277} is an equilibria pressure at T=277 K;

g $x_{CO_2}^h$ is a mole fraction CO_2 in hydrate phase;

h S_t is an equilibria type of structure.

connected with the more suitable size of hydrate small cavities for methane molecules in spite of their weaker interactions with surrounding water molecules. In the Table 1 the data for binary hydrates formation conditions at several temperatures and gas phase compositions are presented. Calculations were performed for equilibria *water–gas–hydrate* (T = 277 K) and for equilibria *ice–gas–hydrate (*T = 273 K, 258 K*).*

At the relatively low pressures, solubility of considered gases in ice and water was neglected in our calculations. As could be expected, the equilibrium pressure in systems *gas–hydrate–ice (water)* increases with temperature and decreases with rising amount of carbon dioxide in gas phase. Analysis of data also shows non-trivial increasing of the carbon dioxide mole fraction in hydrate for decreasing temperature. That can be connected with the lowering formation pressure at temperature decreasing. We can conclude that at low pressure methane is less favorable then carbon dioxide in cavities occupation.

The formation pressure of binary hydrates rises with increasing methane content in the gas phase and increasing temperature. For temperature about 277 K corresponding to water temperature near the bottom of oceans, methane hydrates can form and exist in thermodynamic equilibrium with water and gas at the pressure 4.2 MPa corresponding to 420 meters depth (depths of continental slope) while for one-component hydrate of carbon dioxide the formation pressure is lower, 1.2 MPa. At lower temperatures (273 K, 258 K), decrease of the hydrate formation pressure at addition of carbon dioxide to methane becomes not so significant. Thus, at methane content diminishing from 100% to 0% change in the formation pressure at T = 273 K is about 1.5 MPa and at T = 258 K it is about 0.8 MPa.

(a)   **(b)**
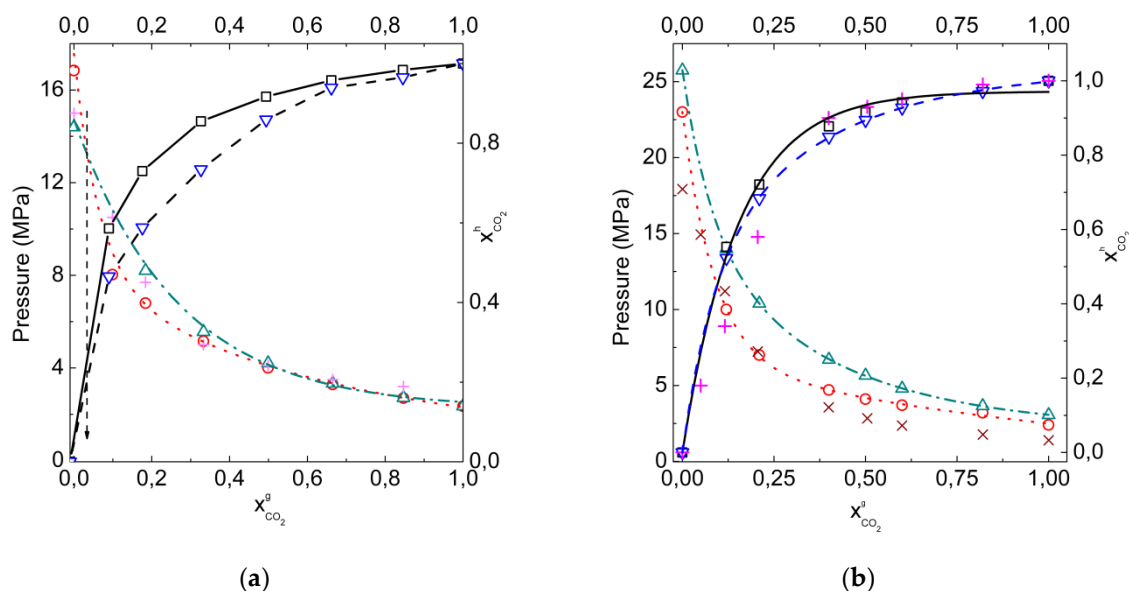
Figure 6. Phase equilibria *gas–hydrate–ice (water)* for carbon dioxide and nitrogen gas mixtures for CS-I and CS-II hydrates in comparison with experimental data (*skew crosses*) [25], (*crosses*) [27] at (a) T = 272 K; (b) T = 274 K respectively (P_{eq}^{CS-I} dotted by open circles, P_{eq}^{CS-II} dash-dotted by open triangles, $x_{CO_2}^{CS-I}$ by solid open square, and $x_{CO_2}^{CS-II}$ by dashed open inverted triangles lines).

With increasing of methane content in the gas phase, the hydrate formation pressure gradually rises. Formation pressure of double hydrates of methane and carbon dioxide has appeared to be a

linear function of the methane content in the hydrate. This is remarkable having in mind significant difference in interaction strengths between guest molecules (carbon dioxide-carbon dioxide, methane-methane).

The conducted calculations of the composition of the formed hydrates at different temperatures have shown that for replacement of methane in hydrate by carbon dioxide the low temperatures are preferable.

To understand the influence of addition nitrogen to carbon dioxide on hydrate formation conditions and compositions, the dependencies of the formation pressure and mole fraction of CO_2 in hydrate on gas phase composition for temperatures T = 272 K (*equilibria gas-hydrate-ice*), and T = 274 K (*equilibria gas-hydrate-water*), and in the range for CO_2 mole fractions from 0.0 to 1.0 in gas phase (Figure6 a, b) were found.

The calculations show that for all gas phase compositions the fraction of CO_2 more than 0.035 is higher in hydrate phase relative to gas phase, hydrate structure CS-I appears to be more stable than structure CS-II. While for all gas phase compositions the fraction of CO_2 less than 0.035 is higher in hydrate phase relative to gas phase, hydrate structure CS-II appears to be more stable than structure CS-I. That could be connected with the greater ratio of large cavities in the CS-I structure what is more suitable for CO_2 molecules. Even at 20% CO_2 in the gas phase CO_2 fraction in hydrate reaches 0.75 at T = 272 K and 0.70 at T = 274 K. As one can see from Figure 6b, experimental data are described with a reasonable accuracy, at least for relatively low temperatures.

The absence of phase transition *CS-I–CS-II* in received results at T = 274 K can be connected with the roughness of used approximation in which we have not taken into account the solubility of gases on water. It is not very important at low pressure but significant at high pressure, when N_2 and CO_2 solubility rapidly increase. On the other hand, the solubility of gases at the ice at formation conditions one can neglect.

The next systems we have considered were CO_2 + CH_4 +N_2 mixtures which can form hydrates with water or ice. In the gas mixture N_2 mole fraction was fixed to be 0.7 and relative content of CO_2 and CH_4 was varying from 0.00 CO_2 to 0.30 CO_2 in the gas phase. On Figure 7a, b calculated formation pressures and mole fractions of guests in hydrates of ternary mixtures CO_2 + CH_4 + N_2 are presented.

(a)   (b)
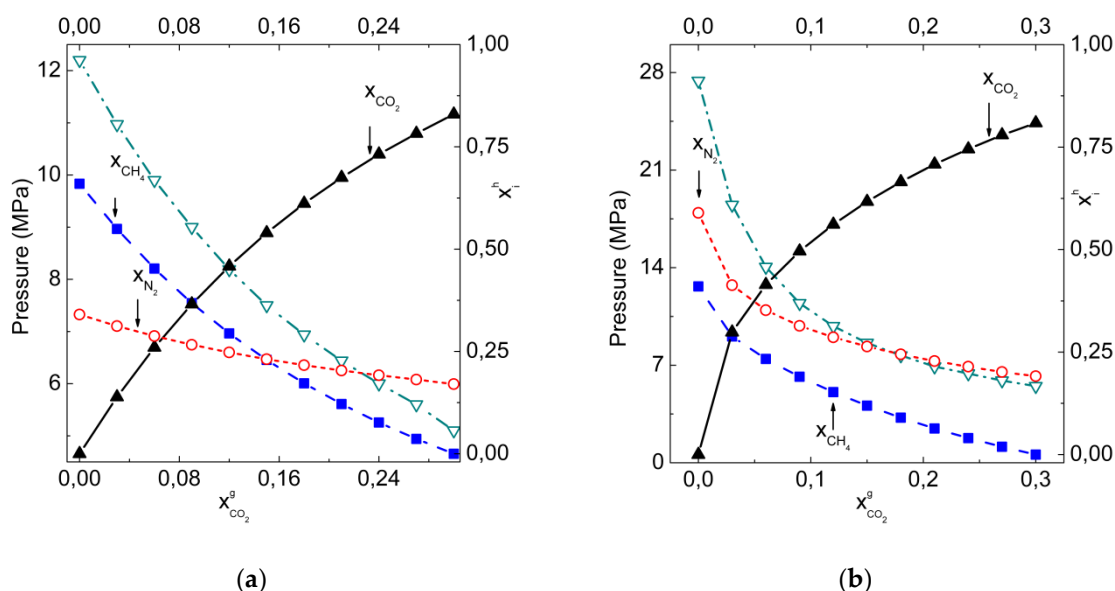
Figure 7. Formation pressure and composition of ternary hydrates carbon dioxide, methane and nitrogen in dependence on carbon dioxide mole fraction in gas phase, nitrogen mole fraction in gas phase was fixed at value 0.7 at temperatures of hydrate formation (a) T = 273 K; (b) T = 277 K (P_{eq} dash dotted by open inverted triangles,x_{CH_4} dashed by filled squares, x_{CO_2} solid by filled triangles, and x_{N_2} dotted by open circles lines).

The mole fraction of CO_2 in hydrate increases rapidly with the growth of its content in the gas phase. The fraction of CO_2 at equilibria both with water and with ice, even at small CO_2 concentrations, is at least three times higher in hydrate phase than in gas mixture (Figure7 a, b). The behavior of N_2 and CH_4 guests at equilibria with ice and water are quite different. At equilibrium with ice, CH_4 occupies much more cavities than N_2 up to 0.15 mole fraction CH_4 in gas phase, while at higher temperatures, at equilibrium with water and thus for higher formation pressures, the nitrogen becomes more suitable for occupation of hydrate small cavities.

Solubility of carbon dioxide in water is comparatively high and reaches one mole/liter at the hydrate formation pressure and temperature (1.24 MPa at 273 K). At these conditions, the methane solubility is not higher than 0.03 mole/liter. So, we can conclude that even at small CO_2 concentrations in gas phase it can be in the excess in reaction mixture what will promote the methane displacement from hydrate.

In the Table 2 the calculated *P-T-x* equilibria conditions of *gas–hydrate–ice (water)* systems at 70% in gas phase are presented.

Table 2. P-T-x equilibria for CO_2+CH_4+N_2 +H_2O *gas–hydrate–ice (water)* systems at 70% N_2 in gas phase.

P^{258}a (MPa)	P^{265}b (MPa)	P^{273}c (MPa)	P^{274}d (MPa)	$x^g_{CO_2}$ e	$x^g_{CH_4}$ f	S^{273}_h g
1.69	1.91	2.76	5.10	0.30	0.00	CS-I
2.08	2.45	3.37	6.44	0.21	0.09	CS-I
2.45	3.00	3.95	7.50	0.15	0.15	CS-I
2.98	3.87	4.74	9.00	0.09	0.21	CS-I
3.97	5.50	6.60	12.20	0.00	0.30	CS-I

a P^{258} is pressure at temperature 258 K;

b P^{265} is pressure at temperature 265 K;

c P^{273} is pressure at temperature 273 K;

d P^{274} is pressure at temperature 274 K;

e $x^g_{CO_2}$ is a mole fraction CO_2 in gas phase;

f $x^g_{CH_4}$ is a mole fraction CH_4 in gas phase;

g S^{273}_h is a type of hydrate structure.

If could be assumed, the formation pressure rises rapidly with the temperature and with lowering CO_2 content in the gas phase. The obtained data show very significant of increase the formation pressure after transition from ice to liquid water.

4. Conclusions

In this work, a method based on the solid solution theory of clathrate hydrate [34-38] has been presented to investigated the effects of influence of nitrogen on the equilibrium pressure and an the hydrate composition of clathrate hydrates formed from methane + carbon dioxide and nitrogen +carbon dioxide binary gas and methane + carbon dioxide + nitrogen ternary gas mixtures. The comparison of degrees of filing for binary CO_2 + CH_4 with ternary CO_2 + CH_4 + N_2 mixed hydrates showed that carbon dioxide molecules occupy both small and large cavities more preferably than methane but in this case of ternary mixed hydrate cavities occupation by N_2 molecules can be concurred by CO_2 and CH_4 molecules.

In all considered systems with and without N_2, at high and medium content of CO_2 in the gas phase we have found that CO_2 is more favorable to occupy clathrate hydrate cavities than CH_4 or N_2. Addition of N_2 to the gas phase increases ratio concentration CO_2 in compressing with

concentration CH_4 in clathrate hydrates and makes gas replacement more effective. The calculation results of the $CO_2 + CH_4$ hydrates confirmed that for all gas phase compositions the fraction of CO_2 is higher in hydrate phase relative to gas phase, hydrate structure CS-I appears to be more stable than structure CS-II. The mole fraction of CO_2 in $CO_2 + CH_4 + N_2$ gas hydrate increases rapidly with the growth of its content in the gas and the formation pressure of $CO_2 + CH_4 + N_2$ gas hydrate rises in comprising with the formation pressure of $CO_2 + CH_4$ gas hydrate. Our calculated data were compared with the experimental data [6,25,47] and it was shown that the used theory generally over predicts the experimental data.

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