

DESCRIPTION OF GAS HYDRATES EQUILIBRIA IN SEDIMENTS USING EXPERIMENTAL DATA OF SOIL WATER POTENTIAL

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ABSTRACT

The purpose of the work is to show how to employ the experimental data from geocryology and soil physics for thermodynamic calculations of gas hydrate phase equilibria by taking into account pore water behavior in sediments. In fact, thermodynamic calculation is used here to determine the amount of non-clathrated pore water content in sediments in equilibrium with gas and hydrate phases.

A thermodynamic model for pore water behavior in sediments is developed. Taking into account the experimental water potential data, the model calculations show good agreement with the experimentally measured unfrozen water content for different pressure and temperature conditions. The proposed thermodynamic model is applied for calculations of three-phase equilibria: multicomponent gas phase (methane, natural gas, etc.) – pore water in clay, sand, loamy sand, etc. – bulk (or pore) hydrate. As a result, correlations have been established between unfrozen and non-clathrated water content in natural sediments.

Keywords: gas hydrates, unfrozen and non-clathrated water, sediment, thermodynamic simulation

NOMENCLATURE

c	heat capacity	[J/mol·K]	W	water content	%
C	Langmuir constant	[MPa ⁻¹]	x	gas molar fraction	-
f	fugacity	[MPa]	γ	hydrate-water interfacial tension	[H/m]
h	enthalpy	[J/mol]	μ	chemical potential	[J/mol]
M	molecular mass	[g/mol]	ν	gas hydrate structure parameter	-
p	pressure	[MPa]	ρ	specific gravity	[g/cm ³]
r	pore radii	[m]	Ψ	water potential	[MPa]
R	universal gas constant	[J/mol K]			
T	temperature	[K]			
V	molar volume	[cm ³ /mol]			

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INTRODUCTION

The first analytical relationship was developed by Makogon between hydrate dissociation pressure and vapor pressure above the pore water surface [1]. A similar method was developed by Chersky, *et al.*, that takes into account the effective pore radii [2]. Using this approach, the decrease of the equilibrium temperature (ΔT) of hydrate decomposition in porous medium has been calculated and compared with that for the bulk hydrate. Depending on the hydrate structure and the hydration ratio it was found that the temperature shift can be in the range of 1.36-1.60 K for capillary water which fills in pores with the radius of $10^{-6} \leq r \leq 10^{-7}$ m. In the case of bound water which occupies pores with radii of $r \leq 10^{-8}$ m, the expected temperature shift can reach 6.8-8.0 K. Later, Tsarev slightly improved this method [3].

Furthermore, Handa and Stupin [4] experimentally observed a shift in the thermodynamic hydrate stability curve to lower temperatures and/or higher pressures with respect to bulk conditions for both methane and propane clathrates in porous silica. Several theoretical models have been put forward [5,6] to explain this behavior. However, in spite of the good qualitative agreement between the model and the existing experiments, a strong quantitative deviation exists between them estimated to be 16 % in the pressure. Similar experiments, but with a wider range of pore sizes, were conducted by Uchida, *et al.* [7]. These experiments confirmed that the effect of porous media on hydrate equilibrium conditions strongly depends on the pore diameter. The pores effect on hydrate stability in natural samples was also investigated by Clennell, *et al.* [8], who suggested a simple model incorporating the pore size.

Recent experiments have been discussed in numerous publications on the effect of narrow interconnected throats between pores on clathrate dissociation conditions in porous media [9-20].

In the majority of these studies, the Gibbs-Thomson relationship for clathrate growth in narrow capillaries has been employed in order to develop thermodynamic models for the prediction of hydrate equilibria in porous media

$$\Delta T/T_d^{bulk} = -4\gamma_{HW}/\rho_H L_H d,$$

where γ_{HW} is the hydrate-water interfacial tension, d is the capillary diameter, ρ_H and L_H are the hydrate specific gravity and enthalpy of clathrate dissociation, respectively.

Most calculations considered only the effect associated with the curvature of the interfacial surface in the pore space, or the so-called capillary pressure effect. Melnikov and Nesterov [21] suggested a model to describe the equilibrium conditions of methane and propane hydrate formation in the pores (capillary effect) and in thin wetting films (disjoining effect). It was determined that the effect of porous media on hydrate phase equilibrium becomes significant for a pore diameter smaller than 1 μm .

The paper's purpose is to improve the available thermodynamic methods for calculation of hydrate phase equilibria, taking into account the properties of pore water in natural sediments (for instance, three-phase equilibrium of "gas – pore water – gas hydrate") in a similar way as for unfrozen water in geocryology science. A number of quantitative techniques (contact-saturation, calorimetric, dielectric, nuclear magnetic resonance, and others) are used for determination of unfrozen water content in sediments and its dependence on temperature variation. (For a detailed description of these experimental methods, please see [22,23]).

The new term "non-clathrated water" is used below. This term denotes a minimal possible amount of pore water in equilibrium with both the bulk hydrate and gas phases in a soil porous sample at the given temperature and gas pressure. The unfrozen water content primarily depends on temperature and only slightly on external pressure. As for non-clathrate water content, it depends on temperature, gas pressure, and gas hydrate-former. The paper's main aim is the application and adaptation of geocryology and soil physics methods for the thermodynamic calculation of non-clathrated water content in sediments. In fact, this paper answers the question of how to estimate the non-clathrated water content if pore water potential is known.

THERMODYNAMICS OF WATER PHASE IN POROUS MEDIA

For further thermodynamic description of pore water, the standard state of water phase is defined as bulk water phase at atmospheric pressure (0.101325 MPa). Thus, for temperatures below 273.15 K the presence of any liquid water phase is defined to be a metastable phase, or so-called supercooled water. According to previous experimental data [24], the supercooled water can exist as bulk phase for temperatures below

~235 K, and its thermodynamic and thermal properties (vapor pressure, heat capacity, etc.) are precisely and reliably determined up to 245-250 K. Furthermore, the bulk hexagonal ice at pressure $p_0 = 0.101325$ MPa and temperature below 273.15 K can be considered as the standard thermodynamic state of pore ice.

Thermodynamic properties of supercooled water

Now introduced are the thermodynamic characteristics of liquid (supercooled) water in respect to hexagonal ice as the functions of temperature at $p_0 = 0.101325$ MPa and $T < 273.15$ K and define the following parameters:

$\Delta\mu_{w,i}^0(T)$ (J/mol) is the difference between chemical potentials of supercooled water and hexagonal ice

$\Delta h_{w,i}^0(T)$ (J/mol) is the difference between supercooled water and hexagonal ice enthalpies

$\Delta c_{w,i}^0(T)$ (J/mol·K) is the difference between supercooled water and hexagonal ice heat capacities

$\Delta V_{w,i}^0(T)$ (cm³/mol) is the difference between supercooled water and hexagonal ice molar volumes.

Here the indexes w and i mean water and ice phases, correspondingly. The same values without upper indexes (⁰) are related to gas (methane or nitrogen) pressure, p , for which $p > p_0$. The inversion of the bottom indexes causes a sign of the thermodynamic parameters to be changed, e.g.,

$$\Delta\mu_{w,i}^0(T) = -\Delta\mu_{i,w}^0.$$

It should be mentioned that these thermodynamic characteristics can formally be defined for temperatures higher than 273.15 K where they represent the stable water phase and the metastable (superheated) ice phase.

At $T_0 = 273.15$ K and $p_0 = 0.101325$ MPa we have:

$\Delta\mu_{w,i}^0 = 0$, meaning the equilibrium between ice and water

$\Delta h_{w,i}^0 = \Delta h_{w,i}^0(T_0) = 6008.0$ J/mol, calculated using the specific heat of the “water-ice” phase transition of 333.5 kJ/mol and the water molecular mass of 18.015 g/mol

$\Delta c_{w,i}^0 = 36.9328$ J/mol K

$\Delta V_{w,i}^0 = -1.6421$ cm³/mol.

From [24-26] the experimental values are available for heat capacities of hexagonal ice and supercooled water and their dependence on the vapor pressure and other properties of supercooled water and ice. After thermodynamic analysis of these data the following values for saturated vapor pressure of supercooled water and ice presented in Table 1 can be recommended for further use.

Temperature, K	Saturated vapor pressure, Pa×10 ²	
	p_w	p_i
273.15	6.1165	6.1165
273.15	6.1121	6.1115
268.15	4.2184	4.0180
263.15	2.8656	2.5995
258.15	1.9141	1.6534
253.15	1.2558	1.0329
248.15	0.8084	0.6330
243.15	0.5099	0.3802
238.15	0.3147	0.2236

Table 1. Saturated vapor pressures of supercooled water P_w and ice P_i at temperatures below 273.15 K

An analytical approximation for the difference of heat capacities $\Delta c_{w,i}^0(T)$ between supercooled water and hexagonal ice, obtained by processing of the experimental data, is:

$$\Delta c_{w,i}^0 = \Delta c_{w,i}^0(T) = 36.9328 + 28.3542 \cdot 10^{-6} (T - T_0)^4, \text{ J/mol} \cdot \text{K}$$

at $T \leq T_0 = 273.15$ K.

The difference between supercooled water and ice chemical potentials $\Delta\mu_{w,i}^0 = \Delta\mu_{w,i}^0(T)$ as a function of temperature can be obtained from the saturated vapor pressures of supercooled water using the following relation:

$$\Delta\mu_{w,i}^0 = \Delta\mu_{w,i}^0(T) = RT \ln \frac{p_w(T)}{p_i(T)} + 0.101325 \cdot \Delta V_{i,w}^0.$$

Taking into account $\Delta c_{w,i}^0(T)$ and $\Delta h_{w,i}^0$ it is also possible to define $\Delta\mu_{w,i}^0(T)$ as:

$$\frac{\Delta\mu^0(T)}{RT} = \frac{\Delta\mu^0(T)}{RT_0} - \int_{T_0}^T \frac{\Delta h^0(t)}{Rt^2} dt, \quad (1)$$

$$\Delta h(T) = \Delta h(T_0) + \int_{T_0}^T \Delta C_p(t) dt.$$

This study found that the experimental data for saturated vapor pressure and the thermophysical properties of supercooled water and ice are very

close to the theoretically calculated data for the following simplified form of $\Delta\mu_{w,i}^0(T)$:

$$\Delta\mu_{w,i}^0 = \Delta\mu_{w,i}^0(T) = 6008 (1 - T/T_0) - 38.2 \cdot \left[T \ln \frac{T}{T_0} + (T_0 - T) \right] \quad (2)$$

This simplified relation will be used further in these calculations. The estimated error of Eq. 2 does not exceed several percent in the temperature range of 248 – 273 K.

Using the relation:

$$\Delta h(T) = \Delta h(T_0) + \int_{T_0}^T \Delta C_p(T) dT,$$

the difference can be obtained between the molar enthalpies of supercooled water and ice $\Delta h_{w,i}^0 = \Delta h_{w,i}^0(T)$.

The difference between the water and ice molar volumes can be estimated as:

$$\Delta V_{w,i} = -37.0605 \cdot t^2 + 164.2067 \cdot 10^{-2},$$

$$\text{where } t = \frac{T - T_0}{T_0} = \frac{T - 273.15}{273.15}.$$

Now consider the effect of external pressure, p , on $\Delta\mu$ and Δh . For the problems under consideration (the gas hydrate equilibrium with pore water or the influence of external pressure on the shift of unfrozen water curve) the range of gas pressure can be defined as 0.1-20 MPa. As a first approximation in this pressure range it is possible to neglect the effect of $\Delta V_{w,i}$ and $\Delta c_{w,i}^0$ on pressure. However, it is necessary to take into account this effect under higher pressures.

Using the above assumptions, the external pressure effect on $\Delta\mu$ and Δh can be written as follows:

$$\begin{aligned} \Delta\mu_{w,i}(p) &\approx \Delta\mu_{w,i}^0 + \Delta V_{w,i}^0 \cdot (p - p_0), \\ \Delta h_{w,i}(p) &\approx \Delta h_{w,i}^0 + \Delta V_{w,i}^0 \cdot (p - p_0). \end{aligned} \quad (3)$$

Thermodynamic properties of pore water and pore ice in sediments

Let W be the water content of the sediment sample measured in the weight percentage with respect to dry sample weight. Similar to the supercooled water, let us introduce the following thermodynamic characteristics of pore water in sediments (again at standard pressure, $p_0 = 0.1013$ MPa):

$\Delta\mu_{w,wp}^0(T, W)$ (J/mol) is the difference between chemical potentials of bulk (including supercooled) and pore water

$\Delta h_{w,wp}^0(T, W)$ (J/mol) is the difference between bulk and pore water enthalpies (called differential wettability enthalpy)

$\Delta c_{w,wp}^0(T, W)$ (J/mol·K) is the difference between bulk and pore water heat capacities

$\Delta V_{w,wp}^0(T, W)$ (cm³/mol) is the difference between bulk and pore water molar volumes.

It should be noted that $\Delta h_{w,wp}(T, W) \rightarrow 0$, when water content, W , of the sediment sample increases, but in a general case $\Delta h_{w,wp}(T, W) \neq 0$, contrary to the usually used

in geocryology relation $\Delta h_{w,wp}(T, W) = 0$. For

$\Delta c_{w,wp}(T, W)$ in many cases it can be assumed that $\Delta c_{w,wp}(T, W) \approx 0$ ($\Delta c_{w,wp}(T, W) \neq 0$

only if the water content of the sample is extremely small). Therefore, in a temperature range from 260 to 300 K it is possible to accept

$\Delta h_{w,wp}(T, W) = \Delta h_{w,wp}(W)$ for the majority of practical problems. However, it is necessary to

keep in mind that $\Delta h_{w,wp}(W)$ has a strongly nonlinear dependence on water content of the sample and $\Delta h_{w,wp}(T, W) \approx 0$ only in the case of high water content.

Using Eq. 1 the thermodynamic correlations between the introduced values under atmospheric pressure can be represented as:

$$\begin{aligned} \frac{\Delta\mu_{w,wp}^0(T_2, W)}{RT_2} &= \frac{\Delta\mu_{w,wp}^0(T_1, W)}{RT_1} - \int_{T_1}^{T_2} \frac{\Delta h_{w,wp}^0(t, W)}{Rt^2} dt \\ \Delta h_{w,wp}^0(T_2, W) &= \Delta h_{w,wp}^0(T_1) + \\ &+ \int_{T_1}^{T_2} \Delta c_{wpow,w}^0(t, W) dt \approx \Delta h_{w,wp}^0(W). \end{aligned} \quad (4)$$

Assuming that $\Delta c_{w,wp}^0(T, W) \approx 0$,

$$\begin{aligned} \frac{\Delta\mu_{w,wp}^0(T_2, W)}{T_2} &\approx \frac{\Delta\mu_{w,wp}^0(T_1, W)}{T_1} - \\ &- \Delta h_{w,wp}^0 \left(\frac{1}{T_1} - \frac{1}{T_2} \right). \end{aligned} \quad (5)$$

Eq. 5 allows us to recalculate the experimental data on the water chemical potential for different temperatures (i.e., from positive to negative

temperatures in Celsius). Moreover, it follows from Eq. 5 that in the case of high water content (when $\Delta h_{w, wpor}(T, W) \approx 0$), the temperature dependence of the difference between the pore and bulk water chemical potentials becomes

$$\frac{\Delta\mu_{w, wpor}^0(T_2, W)}{T_2} = \frac{\Delta\mu_{w, wpor}^0(T_1, W)}{T_1}.$$

Concerning the estimations for $\Delta V_{w, wpor}(T, W)$ contradictory experimental data appears in the available literature. It follows from general physical and chemical reasons that the value of $\Delta V_{w, wpor}(T, W)$ should be close to zero for capillary water. However, it should differ from zero for both adsorbed water (at least for three or four molecular layers adsorbed on the surface) and for interlayer water in swelling clays. The partial molar volume of interlayer water for swelling clay can be estimated from X-ray diffraction data. The partial volume of adsorbed water can be found from the geometrical analysis.

Knowing $\Delta\mu_{w, wpor}(T, W)$ it is possible to calculate thermodynamic equilibria of pore water with bulk ice or bulk gas hydrate (see below).

Similar to pore water the following thermodynamic values can be introduced for the description of pore ice thermodynamics:

$$\Delta\mu_{i, ipor}(T, W), \Delta h_{i, ipor}(T, W), \Delta c_{i, ipor}(T, W), \Delta V_{i, ipor}(T, W). \quad (6)$$

The following question arises: what is W in this case? It should be noted that the existence of pore ice without pore water is impossible. As a result, in Eq. 6 W can be considered as the liquid pore water content as it is introduced for the pore water, but the presence of a small amount of solid phase (disperse ice) can be assumed. This statement means that $\Delta\mu_{i, ipor}(T, W) = \Delta\mu_{w, ipor}$. For practical purposes assume that $\Delta c_{i, ipor}(T, W) \approx 0$ and $\Delta V_{i, ipor}(T, W) \approx 0$.

This approach does not take into account the thermodynamics of pore ice in sediments. However, it would be interesting to consider this case for the interpretation of the unfrozen water data obtained in the calorimeter study and its comparison with the direct contact-saturation method data. Similar definitions can be used for the description of pore hydrate thermodynamics in

sediments compared to bulk gas hydrate phase (at least for so-called empty hydrate lattice).

Phase equilibria of pore water

Pore water phase equilibrium with bulk ice and gas hydrate phases is considered below.

Strictly speaking, two values of chemical potential (in other words, two values of vapor pressure for pore water) can be introduced for the same water content of the sample depending on whether the thermodynamic system moves along the adsorption or desorption curve. This hysteresis is unimportant for real soil systems, but is intended for special artificial capillary media such as porous glasses. Similar to geocryology science, only the desorption curve will be considered when dealing with the unfrozen water content. It is assumed that the internal equilibrium of pore water takes place in sediment sample (that is, all parts of the moistened sample have the same pore water chemical potential).

As a first step, consider the phase equilibrium between pore water and bulk ice under atmospheric pressure and temperature $T \leq T_0$. At such equilibrium the water and ice chemical potentials in pore space are equal to each other

$$\mu_{wpor}^0(T, W) = \mu_i^0(T)$$

or

$$\Delta\mu_{w, wpor}^0(T, W) = \Delta\mu_{w, i}^0(T).$$

From Eq. 2 we find:

$$\Delta\mu_{w, wpor}^0(T, W) = 6008 (1 - T / T_0) - 38,2 \cdot \left[T \ln \frac{T}{T_0} + (T_0 - T) \right]. \quad (7)$$

If $\Delta\mu_{w, wpor}^0(T, W)$ for the sediment sample is known from the experimental data (see further discussion below), Eq. 7 represents the dependence of the equilibrium water content W of the sample on temperature T (at $T < 273.15$ K). Thus, using Eq. 7 the unfrozen water content can be calculated as a function of temperature. The theoretically calculated data using Eq. 7 should be close to the experimental data of unfrozen water content obtained by the contact-saturation method. It is possible to define the effect of gas pressure on unfrozen water content, that is, equilibrium water content at temperature, T , and pressure, p , from the relations:

$$\begin{aligned}
& \mu_{w,wp\text{or}}(T, W) + V_{w,wp\text{or}}(p - p_0) + RT \ln(1 - x) = \\
& = \mu_i^0(T) + V_i(p - p_0); \\
& \Delta\mu_{w,wp\text{or}}(T, W) - RT \ln(1 - x) + \Delta V_{w,wp\text{or}}(p - p_0) = \\
& = \Delta\mu_{w,i}^0(T) - \Delta V_{i,w}; \\
& \Delta\mu_{w,wp\text{or}}(T, W) - RT \ln(1 - x) + \Delta V_{i,wp\text{or}}(p - p_0) = \\
& = \Delta\mu_{w,i}^0(T),
\end{aligned}$$

where x is the molar fraction of dissolved gas in water under pressure, p , and

$$\Delta V_{i,wp\text{or}}(T, W) = \Delta V_{i,w}(T, W) + \Delta V_{w,wp\text{or}}(T, W).$$

Taking into account Eq. 2, the equation for the calculation of the unfrozen water content under gas pressure p can be written as:

$$\begin{aligned}
& \Delta\mu_{w,wp\text{or}}^0(T, W) - RT \ln(1 - x) + \Delta V_{i,wp\text{or}}(p - p_0) = \\
& = 6008(1 - T/T_0) - 38,2 \cdot \left[T \ln \frac{T}{T_0} + (T_0 - T) \right] \quad (8)
\end{aligned}$$

The value x is the solubility of gas in water under pressure p , which can be defined by the Henry law (in its thermodynamic generalization called Krichevskii - Kazarnovskii equations), which incorporates Henry's coefficients and partial molar volumes of gases dissolved in water. These values are well known for many gases, such as hydrocarbons, inert gases, and others, from the experimental data on gas solubility in bulk water. For the gas solubility in this case of pore water, the same Henry's coefficients can be used approximately by introducing a small correction for the so-called "insoluble volume" if needed. Pore water mineralization can also be taken into account through an additional term defined by the Pitzer method, which can be included in Eq. 8 as a changing water activity in solution.

Similar relations can be written for bulk gas hydrate as for the bulk ice phase. In the case of gas hydrate, pressure is created by hydrate-forming gas. When the phase equilibrium of "pore water - gas - bulk hydrate" takes place at temperature T and pressure p , the chemical potentials of liquid water $\mu_{w,wp\text{or}}(T, W, p)$ and hydrate $\mu_h(T, p)$ become equal:

$$\begin{aligned}
& \mu_{w,wp\text{or}}(T, w, p) = \mu_h(T, p), \\
& \Delta\mu_{w,wp\text{or}}(T, W, p) = \Delta\mu_{w,h}(T, p), \quad (9)
\end{aligned}$$

where $\Delta\mu_{w,h}(T, p)$ is the difference between chemical potentials of water in liquid and gas hydrate phases.

As a result, this is obtained:

$$\begin{aligned}
& \Delta\mu_{w,wp\text{or}}(T, W, p) = \Delta\mu_{w,wp\text{or}}^0(T, W) + \\
& + \Delta V_{w,wp\text{or}}^0 \cdot (p - p_0) \quad (10)
\end{aligned}$$

In major cases of practical interest $\Delta V_{w,wp\text{or}}^0 \approx 0$ and $\Delta\mu_{w,wp\text{or}}^0(T, W)$ can be assumed as a known value that can be determined from the experimental data (see below).

The correlations for $\Delta\mu_{w,h}(T, p)$ can be written using the classic van-der-Waals and Barrer thermodynamic model for clathrate solution:

$$\begin{aligned}
& \Delta\mu_{w,h}(T, p) = \Delta\mu_{w,h}^0(T) + \Delta V_{h,w}^0 \cdot (p - p_0) + \\
& + RT \left[\nu_1 \ln \left(1 + \sum_k C_{1,k}(T) f_k \right) + \nu_2 \ln \left(1 + \sum_k C_{2,k}(T) f_k \right) \right] = \\
& = \Delta\mu_{h,w}^0(T) - \Delta V_{h,w}^0 \cdot (p - p_0) + \\
& + RT \left[\nu_1 \ln \left(1 + \sum_k C_{1,k}(T) f_k \right) + \nu_2 \ln \left(1 + \sum_k C_{2,k}(T) f_k \right) \right], \quad (11)
\end{aligned}$$

$$\frac{\Delta\mu_{h,w}^0(T)}{RT} = \frac{\Delta\mu_{h,w}^0(T_0)}{RT_0} - \int_{T_0}^T \frac{\Delta h_{h,w}^0(t)}{Rt^2} dt,$$

$$\Delta h_{h,w}^0(T) = \Delta h_{h,w}^0(T_0) + \int_{T_0}^T \Delta c_{h,w}^0(t, W) dt. \quad (12)$$

Here ν_i is the parameters of gas hydrate crystalline structure ($\nu_1 = 1/23$, $\nu_2 = 3/23$ for gas hydrate cubic structure I and $\nu_1 = 2/17$, $\nu_2 = 1/17$ for gas hydrate cubic structure II); f_k is the fugacity of k-component of gas phase (the gas phase is considered as a multicomponent gas mixture); $\Delta V_{h,w}^0 = 4.6 \text{ cm}^3/\text{mol}$ for gas hydrate cubic structure I, $\Delta V_{h,w}^0 = 5.0 \text{ cm}^3/\text{mol}$ for gas hydrate cubic structure II; and $C_{1,k}$, $C_{2,k}$ are Langmuir constants for k-component of the gas phase for small and large cavities in clathrate phases ($C_{1,k}$, $C_{2,k}$ were used for different gases from [27]).

The values of $\Delta\mu_{h,w}^0(T_0)$ and $\Delta h_{h,w}^0(T_0)$ for the thermodynamic properties of empty metastable hydrate lattice are taken from Handa and Tse parameterization [28]:

$$\Delta\mu_{h,w}^0(T_0) = 1287 \text{ J/mol K};$$

$$\Delta h_{h,w}^0(T_0) = 931 \text{ J/mol K} \quad \text{for hydrate cubic structure I and}$$

$$\Delta\mu_{h,w}^0(T_0) = 1068 \text{ J/mol K};$$

$\Delta h_{h,w}^0(T_0) = 764 \text{ J/mol K}$ for hydrate cubic structure II.

The difference between the empty lattice and bulk water heat capacities can be found using an approximation that heat capacity of hexagonal ice is the same as the hydrate empty lattice.

Using Eqs. 9-12, the equation for the calculation of three phase equilibrium of “pore water – gas – bulk gas hydrate” can be written as

$$\begin{aligned} & \Delta \mu_{w,wp\text{or}}^0(T, W) + RT \ln \left(1 - \sum_k x_k \right) + \Delta V_{w,wp\text{or}}^0 \cdot (p - p_0) = \\ & = -\Delta \mu_{h,w}^0(T) - \Delta V_{h,w}^0 \cdot (p - p_0) + \\ & + RT \left[\nu_1 \ln \left(1 + \sum_k C_{1,k}(T) f_k \right) + \nu_2 \ln \left(1 + \sum_k C_{2,k}(T) f_k \right) \right], \end{aligned} \quad (13)$$

where x_k is the molar fraction of k-component in gas mixture dissolved in pore water phase (calculated from the Krichevskii - Kazarnovskii equation).

Using Eq. 13 the equilibrium pressure p (at the given temperature T) can be calculated at the moment when bulk hydrate starts to form, that is, the equilibrium of “pore water - gas - bulk gas hydrate” occurs. (Generally speaking, it is easy to generalize Eq. 13 to take into account the pore hydrate phase in sediment instead of the bulk hydrate phase, which will correspond with the “metastable equilibrium” of “pore water – gas – pore hydrate”). However, in this case additional experimental data is needed (primarily the calorimetric data) for the characterization of the pore hydrate thermodynamic properties with respect to the bulk hydrate phase.

THERMODYNAMIC PROPERTIES OF PORE WATER OBTAINED FROM EXPERIMENTAL DATA ON SOIL WATER POTENTIAL

The experiments were conducted using Water Potential Meter WP 4T. The description of WP 4T can be found in [29]. A detailed description of the experimental result is presented in the other paper of these proceedings [30]. Using this experimental setup can determine the pore water potential ψ (measured in MPa) as a function of temperature and water content (in a temperature range of 5 ÷ 40 °C):

$$\psi = RT \frac{\rho}{M} \ln \frac{p_{wp\text{or}}}{p_w}, \quad (14)$$

where $p_{wp\text{or}}$ is the water vapor pressure (on air) in the sample with water content W (under atmospheric pressure), p_w is the saturated vapor pressure at the sample temperature, R is the universal gas constant, T is the Kelvin temperature of the sample, M is the molecular water mass (18.015 g/mol), and ρ is the specific gravity of pure water at the given temperature ($\sim 1.0 \text{ g/cm}^3$).

The experimental data obtained by WP 4 allows for calculation of the difference between chemical potentials of pore and bulk water $\Delta \mu_{wp\text{or},w}(T, W)$ for the samples with various water content as

$$\Delta \mu_{wp\text{or},w}(T, W) = \psi \frac{M}{\rho}, \quad (15)$$

where M is the molecular water mass (18.015 g/mol), ψ is the water potential (MPa) and ρ is the specific gravity (g/cm^3).

Please note that

$$\Delta \mu_{wp\text{or},w}(T, W) = -\Delta \mu_{w,wp\text{or}}(T, W).$$

Knowing $\Delta \mu_{wp\text{or},w}(T, W)$ gives us an opportunity to calculate the “pore water – gas – bulk gas hydrate” equilibrium conditions for different pore water contents.

The calculated chemical potential difference $\Delta \mu_{wp\text{or},w}$ versus temperature for kaolinite clay obtained from the experimental data on water potential ψ is presented in Fig. 1.

It is obvious from Fig. 1 that

- the dependence of $\Delta \mu_{wp\text{or},w}$ on T is linear in the studied range of temperature and water content, so that $\Delta c_{w,wp\text{or}}^0(T, W) \approx 0$ and $\Delta h_{w,wp\text{or}}^0(T, W) = \Delta h_{w,wp\text{or}}^0(W)$
- $\Delta h_{w,wp\text{or}}^0(W)$ can be calculated using the slope of these linear dependences
- when W decreases the slope increases
- in the case of large W the dependence becomes non-linear meaning that $\Delta h_{w,wp\text{or}}^0(W) \rightarrow 0$, when W increases.

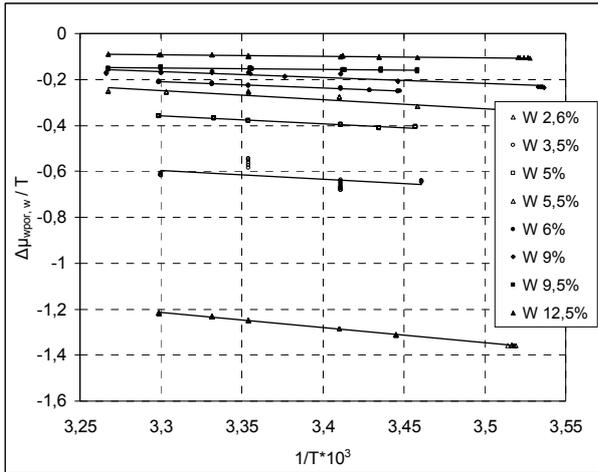


Figure 1. Kaolinite clay. Difference between chemical potentials $\Delta\mu_{wpor,w}$ of pore and bulk water versus temperature (T) for samples with various water content (W, %)

The difference between pore and bulk water chemical potentials calculated from these experimental data at T=293.15 K and 273.15 K are shown in Table 2 and Fig. 2.

W, % (mass.)	$\Delta\mu_{wpor,w}$, J/mol·K	
	at 273.15 K	at 293.15 K
1.8	-630.4	-619.2
2.6	-397.0	-377.1
3.5	-200.9	-194.3
5.0	-131.1	-116.2
9.0	-62.4	-51.3
12.5	-31.9	-29.5

Table 2. Average values of $\Delta\mu_{wpor,w}(W)$ at 273.15 and 293.15 K from the experimental data for kaolinite clay

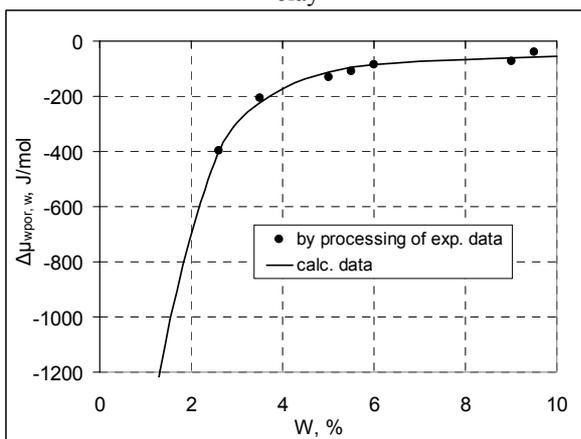


Figure 2. Comparison of the chemical potential difference between pore and bulk water at T=273.15 K theoretically calculated (line) and obtained from the experiment (points)

Fig. 2 uses the analytical approximation:

$$\Delta\mu_{wpor,w} = -24,61051 - \frac{1747,2284}{W^{1,75}}$$

The smoothed values of $\Delta\mu_{wpor,w}$ versus water content, W, at T=273.15 K are presented in Table 3.

W, %	$\Delta\mu_{wpor,w}$, J/mol·K
1.0	-170
1.5	-880
2.0	-540
2.5	-380
3.0	-280
4.0	-180
5.0	-130
6.0	-101
7.0	-83
8.0	-71
9.0	-62
10.0	-56
13.0	-30

Table 3. The chemical potential difference between pore and bulk water versus water content at T=273.15 K (calculation data)

The difference between pore and bulk water enthalpies $\Delta h_{wpor,w}$ can also be calculated from the experimental results and presented in Table 4 and Fig. 3.

W, % (mass.)	$\Delta h_{wpor,w}$, J/mol·K
1.8	-791.6
2.6	-662.7
3.5	-385.7
5.0	-334.8
9.0	-163.0
12.5	-67.2

Table 4. Average values of $\Delta h_{wpor,w}(W)$ from the experiment

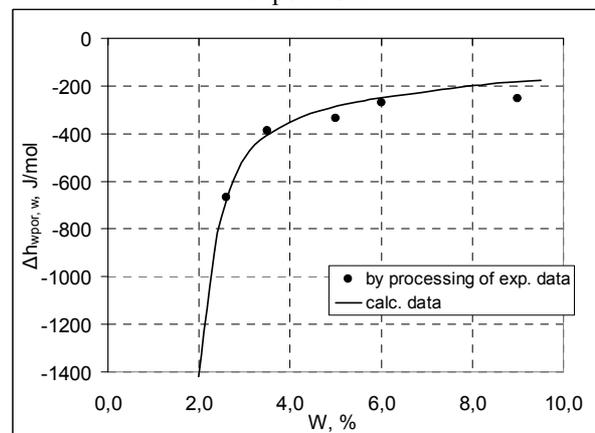


Figure 3. The difference between bulk and pore water enthalpies $\Delta h_{wpor,w}$ versus water content (W) for the kaolinite clay sample

For $\Delta h_{wpor,w}(W)$ the following analytical approximation can be used:

$$\Delta h = 380,667 - \frac{1584,303}{W^{0.5}}$$

The approximated values of $\Delta h_{wpor,w}$ are presented in Table 5.

W, %	$\Delta h_{wpor,w}$, J/mol
1.0	-1200
1.5	-910
2.0	-740
2.5	-620
3.0	-530
4.0	-410
5.0	-330
6.0	-270
7.0	-220
8.0	-180
9.0	-160
13.0	-60

Table 5. Difference between bulk and pore water enthalpies $\Delta h_{wpor,w}$ versus water content (W) (calculation data)

THERMODYNAMIC CALCULATIONS OF PORE WATER PHASE EQUILIBRIA

Using $\Delta \mu_{wpor,w}^0(T_0, W)$, $\Delta h_{wpor,w}^0(T_0, W)$ and $\Delta c_{wpor,w}^0(T_0, W)$ calculated in the previous section, the thermodynamic calculations can be performed on phase equilibrium of unfrozen or non-clathrated water content in the kaolinite clay sample under gas pressure. The following approximations were used:

$$\Delta c_{wpor,w}^0(T_0, W) \approx 0,$$

$$\Delta h_{wpor,w}^0(T, W) = \Delta h_{wpor,w}^0(T_0, W) \text{ and Eq. 5.}$$

In Fig. 4 the unfrozen water content was compared, which was experimentally measured using the contact-saturation method and presented by points and the thermodynamic calculation (lines) based on the chemical potential of pore water in kaolinite clay sample (see Tables 3, and 5 and Eq. 5). A good agreement can be seen among these data, especially in the 260 - 270 K temperature range of the intensive phase transition of "water – ice".

As a result, using the dew-point device WP 4T a new express method was formulated to measure the unfrozen water content in sediment. This method is presented here.

The next step is the calculation of non-clathrated water content by considering the same data on pore water chemical potential and its comparison

to the experimental data on the non-clathrated water content in the kaolinite clay sample under methane (or carbon dioxide) gas pressure.

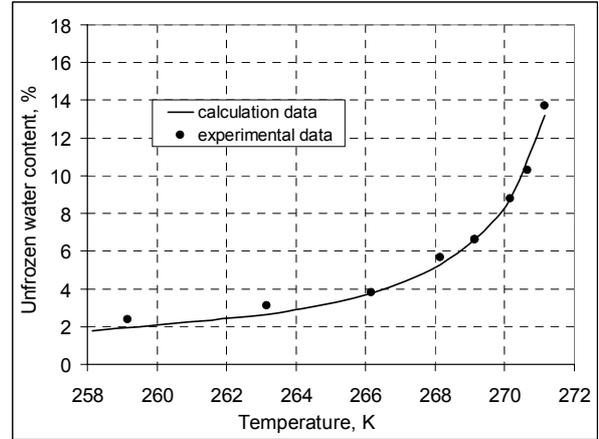


Figure 4. Unfrozen water content for kaolinite clay measured by the contact-saturation method and the calculation data

Let's start with the thermodynamic calculation of "CH₄ gas phase – pore water in kaolinite clay – gas hydrate of structure I" equilibrium at different temperatures with the step of 2.5 degrees from -10 up to +10 °C. To perform this calculation, first determine the pressure and temperature dependence of methane hydrate equilibrium condition with water and ice including the metastable states: supercooled water and superheated ice.

For "CH₄ gas phase – liquid water – gas hydrate structure I" equilibrium the following analytical dependencies can be used:

$$\ln p \text{ (MPa)} = 26.86444 - \frac{7080.1932}{T}$$

at 263.15 K < T < 273.15 K, and

$$\ln p \text{ (MPa)} = 29.11273 - \frac{7694.3008}{T}$$

at 273.15 K < T < 283.15 K

For "CH₄ gas phase – ice – gas hydrate structure I" equilibrium the following analytical dependence can be used:

$$\ln p \text{ (MPa)} = 8.9720 - \frac{2196.62}{T}$$

at 263.15 K < T < 278.15 K

The calculation of the equilibrium non-clathrated water content was done using the data obtained on water chemical potential in kaolinite clay as a function of the water content and temperature (see

Tables 3 and 5). The results are presented in Fig. 5.

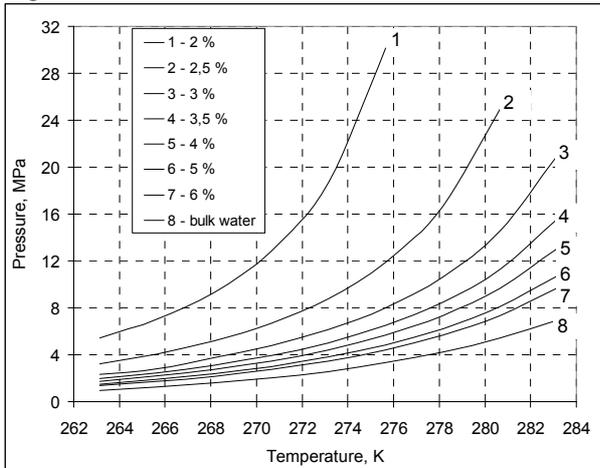


Figure 5. Equilibrium pressure of methane hydrate formation in kaolinite clay at the given water content and fixed temperatures in the range 263 – 283 K

In [30] the non-clathrated water content dependence on methane pressure at the fixed temperature of 265.65 K for the kaolinite clay sample was experimentally measured using the contact-saturation method temperature, Table 6. In Fig. 6 these measured data are compared with the calculation. A good qualitative agreement is seen between the calculation and experimental data; that is, the higher the pressure at the fixed temperature, the smaller the non-clathrated water content, which is in equilibrium with bulk methane gas hydrate. Unfortunately, a solid quantitative fit could not be obtained on the experimental data, but this will be the focus of further study. In our opinion, the experimental technique of hydrate equilibrium determination with pore water needs further improvement.

Non-clathrated water content, %	Pressure, MPa
1.36	8.69
1.44	7.35
1.47	6.85
1.51	5.90
1.68	4.34
2.00	3.10
1.95	3.10
2.38	2.59
3.09	1.83
3.19	1.83
3.80	0.10

Table 6. Pressure influence on non-clathrated water content in kaolinite clay at the fixed temperature 265.65 K (experimental data)

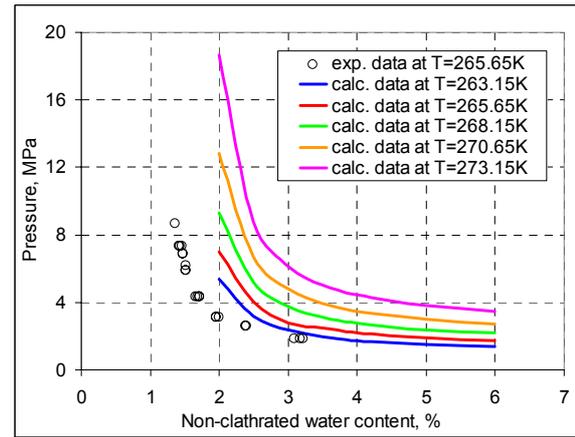


Figure 6. Experimental data obtained by the contact-saturation method at T=265.65 K (points) and the thermodynamically calculated data from water potential (lines) for kaolinite clay

Experimental data on the non-clathrated water content in kaolinite clay at the fixed average pressure of about 4.15 MPa are shown in Table 7. Fig. 7 presents the comparison between experimental and calculation data.

Temperature, K	P, MPa	W, %
271.95	4.2	2.42...2.57
269.98	4.11	2.26...2.28...2.28
265.65	4.34	1.68...1.71...1.71
262.55	4.20	1.63...1.62

Table 7. Temperature influence on non-clathrated water content in kaolinite clay under methane pressure (experimental data)

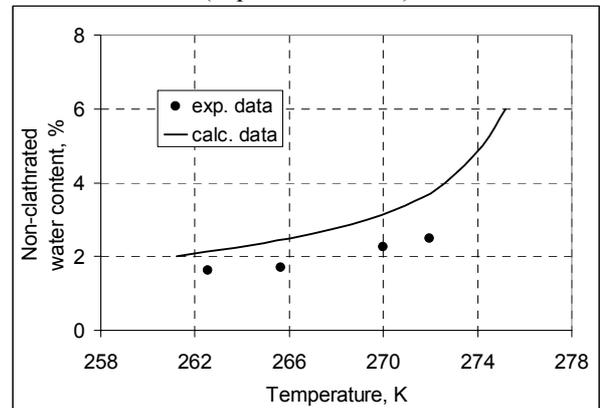


Figure 7. Temperature influence on non-clathrated water content in kaolinite clay under methane pressure (P=4.1- 4.3 MPa)

The proposed method provides an opportunity to calculate the equilibrium amount of non-clathrated water for different gases and their mixtures. The pressure effect on non-clathrated water content for methane and natural mixture, that form structure II hydrates, is illustrated in fig. 8.

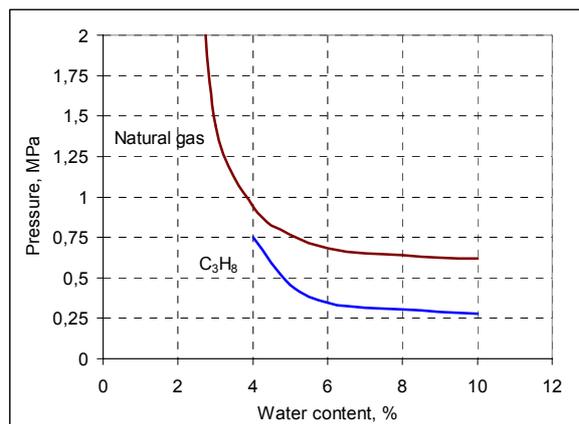


Figure 8. Pressure conditions of gas hydrate (structure II) formation in kaolinite clay versus water content at $T=273.15$ K (Natural gas composition: CH_4 86 mol.%; C_2H_6 6.0 mol.%; C_3H_8 5.0 mol.%; $i\text{-C}_4\text{H}_{10}$ 2.0 mol.%; $n\text{-C}_4\text{H}_{10}$ 1.0 mol.%)

CONCLUSIONS

1. A thermodynamic model has been developed for pore water behavior in natural sediments. This model has been used for estimation of the unfrozen water content based on the experimental measurements of water potential, ψ , as a function of water content in the clay sample. The unfrozen water content data calculated from potential ψ and directly measured by the contact-saturation method are in good agreement for kaolinite clay samples.
2. A thermodynamic model has also been developed for the calculation of three-phase equilibrium: "multicomponent gas phase (methane, natural gas, etc.) – pore water in sediments (clay, sand, loamy sand, etc.) – bulk hydrate". This method allows estimating the equilibrium non-clathrate water content both above and below the zero Celsius temperature.

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