Temperature and pressure correlation for volume of gas hydrates with crystal structures sI and sII

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Abstract. The temperature and pressure correlations for the volume of gas hydrates forming crystal structures sI and sII developed in previous study [Fluid Phase Equilib. 427 (2016) 268-281], focused on the modeling of pure gas hydrates relevant in CCS (carbon capture and storage), were revised and modified for the modeling of mixed hydrates in this study. A universal reference state at temperature of 273.15 K and pressure of 1 Pa is used in the new correlation. Coefficients for the thermal expansion together with the reference lattice parameter were simultaneously correlated to both the temperature data and the pressure data for the lattice parameter. A two-stage Levenberg Marquardt algorithm was employed for the parameter optimization. The pressure dependence described in terms of the bulk modulus remained unchanged compared to the original study. A constant value for the bulk modulus $B_0 = 10$ GPa was employed for all selected hydrate formers. The new correlation is in good agreement with the experimental data over wide temperature and pressure ranges from 0 K to 293 K and from 0 to 2000 MPa, respectively. Compared to the original correlation used for the modeling of pure gas hydrates the new correlation provides significantly better agreement with the experimental data for sI hydrates. The results of the new correlation are comparable to the results of the old correlation in case of sII hydrates. In addition, the new correlation is suitable for modeling of mixed hydrates.

1 Introduction

Our team is developing advanced models for thermophysical properties and phase behavior of fluid and solid systems relevant especially in carbon capture and storage (CCS) technologies. Most of the research is related to the modeling of gas hydrates, i.e. non-stoichiometric solid mixtures of water and various gases. Gas hydrates form so called clathrate structures, in which the hydrogen bonded water molecules build a crystal lattice with cavities containing the gas molecules [1]. Nowadays, gas hydrates are being investigated for several reasons, e.g., in the natural gas industry where they can cause pipeline blockage and other operational failures, as potential energy resource in the form of methane hydrates at the sea bottom or in relation to CCS technologies [2].

A new thermodynamic model for eight gas hydrate formers relevant mostly in CCS has recently been developed by our team [3-5]. The model is based on the van der Waals and Platteeuw approach [6] combined with highly accurate multiparameter equations of state for other phases than the hydrate [7,8]. Pure gas hydrates (water with a single gas species) of carbon dioxide, argon, oxygen, nitrogen, methane, carbon monoxide, ethane and propane can be predicted. An important

advantage of the new model is that it is capable to predict a large variety of phase equilibria including those with pure solid phases, i.e. water ice and solid CO_2 (dry ice), over wide temperature and pressure ranges with very good accuracy. Current activities are focused on a further extension of the pure hydrate model to hydrate mixtures. New complex phase equilibria algorithms, e.g., for three-phase and four-phase equilibria including both fluid and solid phases, are being developed for this purpose [9]. The pure hydrate model also needs to be modified such that it allows consistent modeling of gas hydrates and phase equilibria for various overall compositions of multicomponent aqueous mixtures. Among other, these modifications include a revision of the current correlation for the volume of gas hydrates.

In this study, the volume of gas hydrates forming cubic crystal structures of type sI and sII was investigated. The correlation for the lattice parameter employed in the pure hydrate model [3] was revised and modified such that it can be used for modeling of mixed hydrates. The reference conditions, i.e. the reference temperature T_0 and the reference pressure p_0, of the new volume correlation were set constant for both hydrate structures. Their values $T_0 = 273.15$ K and $p_0 = 1$ Pa are the same as the reference state for the Gibbs energy and enthalpy of hydrate employed in the model for mixed

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hydrates [9]. Parameters of the new correlation for 11 sI hydrates and 18 sII hydrates were correlated to the experimental data for both the temperature and the pressure dependence of the volume of gas hydrates using a two-stage Levenberg–Marquardt algorithm [10,11].

2 Volume of gas hydrates

In case of sI and sII hydrates, the volume can be determined from the lattice parameter a of the unit cell as both structures form a cubic crystal system. In the hydrate models based on the van der Waals and Platteeuw approach [6], a hypothetical crystal structure called empty β-lattice is considered. This structure is formed by water molecules connected through hydrogen bonds and does not contain any gas (guest) molecules in the cavities. Knowing the lattice parameter and the number of water molecules N_w forming the unit cell, which is constant for each hydrate structure, the molar volume of the empty β-lattice can be determined as follows

$$v^{\beta}\left[m^3\,mol^{-1}\right]=\left(a\left[\text{Å}\right]10^{-10}\right)^3\frac{N_{AV}\left[mol^{-1}\right]}{N_w}, \quad (1)$$

where N_{AV} stands for the Avogadro constant. The molar volume of hydrate can be calculated from the molar volume of the empty β-lattice in the following manner

$$v=v^{\beta}\left(1+\sum_i \upsilon_i \sum_J \theta_{i,J}\right)^{-1}. \quad (2)$$

In eq. (2), υ_i is the number of cavities of type i divided by the number of water molecules in a unit cell N_w and $\theta_{i,J}$ is the fractional occupancy of cavity i by guest molecule of type J. The cage occupancy $\theta_{i,J}$ needs to be determined from a convenient hydrate model, e.g., ref. [3-5,12,13] or experimentally by diffraction methods [14-16].

Table 1. Summary of experimental data for the lattice parameter of sI hydrates

Guest	T – data		p – data	
	N	Ref.	N	Ref.
EtO	28	[20,21]	-	
CO₂	70	[16,17, 22-26]	-	
C₂H₆	11	[17]	10	[27]
0.85CH₄ + 0.15 CO₂	4	[17]	-	
0.47 CH₄ + 0.53 C₂H₆	2	[17]	-	
TMO	8	[28]	-	
CO	1	[29]	-	
H₂S	1	[30,31]	-	
CH₄	53	[16,31-36]	52	[37,38]
Xe	26	[16,23,29]	16	[27,39]
N₂ (sI)	-		6	[14,15]

Tables 1 and 2 summarize experimental data points available for the lattice parameter of sI hydrates and sII hydrates, respectively. The annotation "T – data" denotes data for the temperature dependence of the lattice

parameter measured at low pressures below 1 MPa; typically at atmospheric pressure. "p – data" marks data measured at higher pressures up to 3 GPa. Tables 1 and 2 contain also data for several binary mixed hydrates measured mostly by Hester et al. [17].

Table 2. Summary of experimental data for the lattice parameter of sII hydrates

Guest	T – data		p – data	
	N	Ref.	N	Ref.
Air	5	[29,40]	4	[15]
Ar	1	[29]	-	
Kr	3	[30]		
O₂	1	[29]	9	[15]
N₂	18	[16,29]	18	[14,15]
TMO	9	[28]	-	
C₃H₈	21	[17,33,41]	-	
0.60 CH₄ + 0.4 C₃H₈	3	[17]	-	
0.30 C₂H₆ + 0.7 C₃H₈	5	[17]		
0.182 CO₂ + 0.818 C₃H₈	5	[17]		
0.876 CH₄ + 0.124 i-C₄H₁₀	7	[17]		
Natural gas	3	[17]	-	
0.95 CH₄ + 0.05 C₅H₁₀O	10	[17]		
THF	18	[21,42]		
0.82 CH₄ + 0.18 C₂H₆	12	[43]		
THF + H₂S	1	[44]		
THF + Xe	-		13	[27]
CH₄ (sII)	-		13	[45]

2.1 Correlations for the temperature dependence

Most of the hydrate models, e.g., by Klauda and Sandler [46] or Martín and Peters [47], use correlations for the thermal expansion of lattice parameter determined by Tse et al. on the basis of their experimental measurements with ethylene oxide (EtO) hydrates for structure sI [20,21]

$$a(T)=11.835+2.2173\cdot10^{-5}T+2.2415\cdot10^{-6}T^2, \quad (3)$$

and with tetrahydrofuran (THF) hydrates [21] for structure sII

$$a(T)=17.130+2.249\cdot10^{-4}T+ \\ 2.013\cdot10^{-6}T^2-1.009\cdot10^{-9}T^3. \quad (4)$$

Both correlations provide reasonable results over a wide temperature range from 20 K up to 260 K. However, application of eqs. (3) and (4) to the modeling of various hydrates different from ethylene oxide and tetrahydrofuran represents a rather rough simplification. As it is shown later in Tables 5 and 6 in section 3.1, the lattice parameter at a given temperature and pressure may significantly vary for various hydrate formers. The reason is that the interactions between the guest molecules and the water cavities and subsequently the volume of the unit cell depend on the guest type.

A universal and accurate correlation for thermal expansion of sI and sII hydrates was developed by Hester et al. [17]. Based on the literature data and their own experimental measurements for a large variety of hydrates including binary mixed hydrates, Hester et al. found out that the thermal expansion can be considered dependent only on the hydrate structure. Consequently, the temperature dependence of the relative lattice parameter a/a_0 can be universally described by the following function for all hydrates forming the same crystal structure.

$$\frac{a(T)}{a_0} = \exp\left[\begin{array}{c} \alpha_1\left(T-T_0\right) + \\ \alpha_2\left(T-T_0\right)^2 + \alpha_3\left(T-T_0\right)^3 \end{array} \right] \quad (5)$$

In eq. (5), a_0 denotes the lattice parameter at the reference temperature $a(T_0)$. Introduction of the reference lattice parameter in eq. (5) made the correlation by Hester et al. universal for all sI and sII hydrates unlike the correlations by Tse et al. [20,21], eqs. (3) and (4), which are based solely on the data for two specific hydrates.

Hansen et al. [16] have recently measured new accurate data for the thermal expansion of hydrogenated and deuterated hydrates of CO_2, CH_4, Xe and N_2 over wide temperature ranges from 10 K up to the stability limit around 280 K. A high-pressure cell was used for the measurements at the temperatures above 200 K. The data were correlated by polynomial fits of up to the forth order in case of CO_2, CH_4, and N_2 hydrates. The data for Xe hydrates and for CO_2 hydrates (for comparison) were correlated by Hansen et al. [16] by a modified Einstein model for thermal expansion.

$$a(T) = a_0 + (e_0 + e_1 T)/\left[\exp(\theta_E/T) - 1\right] \quad (6)$$

In eq. (6), a_0 is the lattice parameter at 0 K, e_0 and e_1 are coefficients of the internal energy of the crystal, and θ_E is a characteristic Einstein temperature. Correlation (6) provided better results only for Xe hydrates compared to the polynomial fits. Based on their new data, Hansen et al. [16] stated that the thermal expansion depends on the hydrate former and that a universal model for all hydrates forming the same crystal structure proposed by Hester et al. [17] can hardly be justified. On the other hand, major differences between the new data of Hansen et al. and the universal correlation (5) occur mostly in the high temperature region above approximately 220 K. The correlation by Hester et al. [17] was based mostly on the low temperature data as the data above 230 K were rather limited at that time. As a consequence, results of correlation (5) by Hester et al. [17] are more or less pure extrapolation to temperatures above 230 K. In this work, we employed the universal approach of Hester et al. [17], because the new temperature and pressure correlation for the volume of gas hydrates is intended for the modeling of various gas hydrates with large differences in the amount and quality of experimental data for the lattice parameter.

2.2 Correlations for the pressure dependence

The data situation for the pressure dependence of the lattice parameter corresponding to the isothermal compressibility of hydrates is significantly worse compared to the thermal expansion data; see the amount of data points and the number of references indicated with "p – data" in Tables 1 and 2.

Most of the hydrate models use various quadratic or cubic functions of pressure in the correlations of hydrate volume, e.g., the correlation employed by Klauda and Sandler [46] based on the data for methane hydrates

$$a(T,p) = \sqrt[3]{a(T)^3 - 8.006 \cdot 10^{-9}\, p + 5.448 \cdot 10^{-12}\, p^2}\ , \quad (7)$$

where $a(T)$ can be obtained from eqs. (3) or (4) and p denotes the pressure in MPa. The main weakness of similar correlations is that they are valid over limited pressure ranges and their extrapolating behavior is rather questionable, e.g., the compressibility of hydrates can increase with increasing pressure or become negative at a certain pressure.

In the accurate model for natural gas hydrates by Ballard and Sloan [1,12], a constant compressibility κ was considered.

$$a(T,p) = a(T)\exp\left[-\kappa(p - p_0)\right] \quad (8)$$

However, as it is discussed in our previous work [3], Ballard and Sloan correlated the compressibility mostly to the hydrate three-phase equilibrium data and not to the crystallographic data for the lattice parameter. Consequently, in the model of Ballard and Sloan [1,12] the compressibility was employed as a sort of correcting parameter improving the predictive ability of the hydrate model at high pressures. Values of κ differ by several orders of magnitude for various hydrate formers in this case.

In our model for pure CO_2 hydrates [13], a non-constant compressibility was introduced.

$$a(T,p) = a(T)\left[1 - \frac{\kappa_1(p - p_0)}{1 + \kappa_2(p - p_0)}\right]. \quad (9)$$

The compressibility given by eq. (9) is monotonically decreasing to zero at an infinite pressure, which represents physically reasonable behavior. Nevertheless, fitting two parameters κ_1 and κ_2 for the compressibility of various hydrate formers appeared as rather difficult task according to unfavorable situation with the experimental data.

In our previous work [3-5] focused on the development of model for eight pure gas hydrates relevant in CCS, it was shown that the pressure dependence of the volume of sI and sII gas hydrates can be well described with the Murnaghan [18] equation of state for solids. The Murnaghan equation is a simplified version of the Birch-Murnaghan [19] equation, which is commonly used for the representation of experimental lattice parameter data. The Murnaghan equation considers a bulk modulus, i.e. the inverse value of the isothermal compressibility, that is linearly increasing with pressure.

$$B(p) = B_0 + B_0' p = \frac{1}{\kappa(p)} \quad (10)$$

In eq. (10), B_0 is the bulk modulus in Pa at zero pressure and B_0' is a constant bulk modulus derivative.

The Murnaghan equation of state results in the following correlation for the pressure dependence of the lattice parameter

$$a(T,p) = a(T,p_0)\left(\frac{B_0 + B_0' p}{B_0 + B_0' p_0}\right)^{\frac{-1}{3B_0'}}, \quad (11)$$

where the reference pressure p_0 is arbitrarily set to 1 Pa in this study. Based on the comparison of the Murnaghan equation and the Birch-Murnaghan equation, the bulk modulus derivative can usually be taken constant $B_0' = 4$. As it was shown in ref. [3], the pressure data available for hydrates forming structures sI and sII can be well correlated with a constant bulk modulus $B_0 = 10$ GPa. This universal value is also used here.

3 New correlation for the lattice parameter of sI and sII gas hydrates

The new correlation for the lattice parameter intended for modeling mixed hydrates has the same mathematical form as the correlation for pure gas hydrates developed in the previous work [3]; see eq. (12). However, the values of the parameters T_0, p_0, a_0 and coefficients α_1 to α_3 are different for the pure hydrate model and the mixed hydrate model.

$$a(T,p) = a_0\left(\frac{B_0 + 4p}{B_0 + 4}\right)^{\frac{-1}{12}}$$
$$\exp\left[\alpha_1(T - T_0) + \alpha_2(T - T_0)^2 + \alpha_3(T - T_0)^3\right] \quad (12)$$

The volume correlation employed in the pure hydrate model has several disadvantages making it inconvenient for the modeling of mixed hydrates. The correlation uses different values for the reference temperature T_0 for each hydrate structure. Moreover, the reference temperatures and the reference pressure differ from the reference state conditions of the water empty β-lattice at which the reference Gibbs energy and the reference enthalpy are given, i.e. $T_0^\beta = 273.15$ K and $p_0^\beta = 1$ Pa; for more detail see ref. [3-5,9]. In the model of pure gas hydrates, the thermal expansion coefficients α_1 to α_3 were evaluated only from the lattice parameter data for CO_2 hydrates in case of sI structure [13] and taken from Hester et al. [17] in case of sII structure. The CO_2 correlation [13] and the correlation by Hester et al. [17] were evaluated solely from the temperature data. Main advantage of the new correlation (12) is that it can simultaneously be fitted to both the temperature and the pressure data. Consequently, all available data summarized in Tables 1 and 2 can be considered in the evaluation of the reference parameter a_0 and the thermal expansion coefficients α_1 to α_3 in the new correlation (12). As a result, the new correlation shall provide a more reliable and universal prediction for the lattice parameter of a large variety of sI and sII hydrates.

For the purpose of the new mixed hydrate model, a universal reference temperature $T_0 = 273.15$ K and a universal reference pressure $p_0 = 1$ Pa are proposed in eq. (12). The bulk modulus has a constant value of

$B_0 = 10 \cdot 10^9$ Pa for all the selected hydrates. Parameter a_0 and coefficients α_1 to α_3 were determined with the help of a two-stage Levenberg-Marquardt optimization algorithm [10,11]. The main algorithm optimizes values for the thermal expansion coefficients α_1 to α_3, which are universal for a given hydrate structure. For each iteration of the main algorithm, nested Levenberg-Marquardt algorithm optimizes the reference lattice parameter a_0 for each hydrate former. The nested algorithm is called N-times, where N is the number of hydrate formers equal to 11 in case of sI hydrates and 18 in case of sII hydrates; see data summarized in Tables 1 and 2. The Levenberg-Marquardt algorithm optimizes following objective function

$$\sum_{i=1}^{N} w_i \left(a_{\exp,i} - a_{\text{cor},i}\right)^2 = \min, \quad (13)$$

where $a_{\exp}$ is the experimental value and a_{cor} is the correlated value of the lattice parameter. w_i stands for the weight of the given experimental data point. For most data points, the weight was set to unity. The weight was reduced to 0.25 for the data measured with deuterated hydrates, i.e. with heavy water (D_2O), and for high pressure data above 700 MPa. The data for deuterated hydrates by Hansen et al. [16] were not considered in the parameter optimization. The weight for the data taken from the molecular simulations for methane hydrates by Docherty et al. [36] was reduced down to 0.0001.

Table 3 shows a comparison of the average deviation AD defined by eq. (14) and the absolute average deviation AAD given by eq. (15) for the correlation employed in the pure hydrate model [3] and for the new correlation. In case of sI hydrates, the new correlation provides significantly lower AD and AAD. Main reason is that the new correlation was fitted to all available data, while the pure hydrate correlation was correlated only to the temperature dependence for CO_2 hydrates. Results of both correlations are comparable in case of sII hydrates. The new correlation is slightly better.

$$\text{AD} = \frac{1}{N}\sum_{i=1}^{N} a_{\exp,i} - a_{\text{cor},i} \quad (14)$$

$$\text{AAD} = \frac{1}{N}\sum_{i=1}^{N} \left| a_{\exp,i} - a_{\text{cor},i} \right| \quad (15)$$

Table 3. Number of experimental data, absolute deviation AD and average absolute deviation AAD for the correlation used in the model for pure gas hydrates [3] and the new correlation eq. (12)

	Vinš et al. [3]	this study
Structure sI		
N	288	
AD / Å	-1.122	-0.550
AAD / Å	4.316	3.388
Structure sII		
N	179	
AD / Å	-0.449	-0.155
AAD / Å	2.128	2.029

3.1 Final parameters

Table 4 contains the final values for thermal expansion coefficients α_1 to α_3 for hydrate structures sI and sII. The reference temperature T_0 in eq. (12) equals 273.15 K.

The optimized values for the reference lattice parameter a_0 are given in Table 5 for sI hydrates and in Table 6 for sII hydrates. The values are being used in the model for mixed hydrates [9].

Table 4. Thermal expansion coefficients for the lattice parameter of sI and sII gas hydrates correlated by eq. (12)

Struct.	α_1 / K^{-1}	α_2 / K^{-2}	α_3 / K^{-3}
sI	$8.416128 \cdot 10^{-5}$	$7.141596 \cdot 10^{-8}$	$-2.106472 \cdot 10^{-10}$
sII	$7.988807 \cdot 10^{-5}$	$1.686500 \cdot 10^{-7}$	$1.363783 \cdot 10^{-10}$

Table 5. Reference lattice parameter a_0 at 273.15 K and 1 Pa in eq. (12) for sI hydrates

Guest	a_0 / Å
EtO	11.997604
CO_2	11.979675
C_2H_6	12.067015
$0.85 CH_4 + 0.15\ CO_2$	11.978807
$0.47\ CH_4 + 0.53\ C_2H_6$	12.042290
TMO	12.138742
CO	12.017111
H_2S	12.082851
CH_4	11.970005
Xe	11.987297
N_2 (sI)	11.969756

Table 6. Reference lattice parameter a_0 at 273.15 K and 1 Pa in eq. (12) for sII hydrates

Guest	a_0 / Å
Air	17.283598
Ar	17.232725
Kr	17.237294
O_2	17.262769
N_2	17.275606
TMO	17.226661
C_3H_8	17.288930
$0.60\ CH_4 + 0.4\ C_3H_8$	17.313328
$0.30\ C_2H_6 + 0.7\ C_3H_8$	17.276450
$0.182\ CO_2 + 0.818\ C_3H_8$	17.327134
$0.876\ CH_4 + 0.124\ i\text{-}C_4H_{10}$	17.374086
Natural gas	17.313652
$0.95\ CH_4 + 0.05\ C_5H_{10}O$	17.435520
THF	17.334988
$0.82\ CH_4 + 0.18\ C_2H_6$	17.284555
THF + H_2S	17.336587
THF + Xe	17.424193
CH_4 (sII)	17.277118

3.2 Results – temperature dependence

Fig. 1 shows a comparison of the experimental data for the temperature dependence of the lattice parameter of sI hydrates with the correlation by Jäger et al. [13] used in the pure hydrate model [3-5] and the new correlation (12). The deviation of both correlations from the experimental data is provided in Fig. 2.
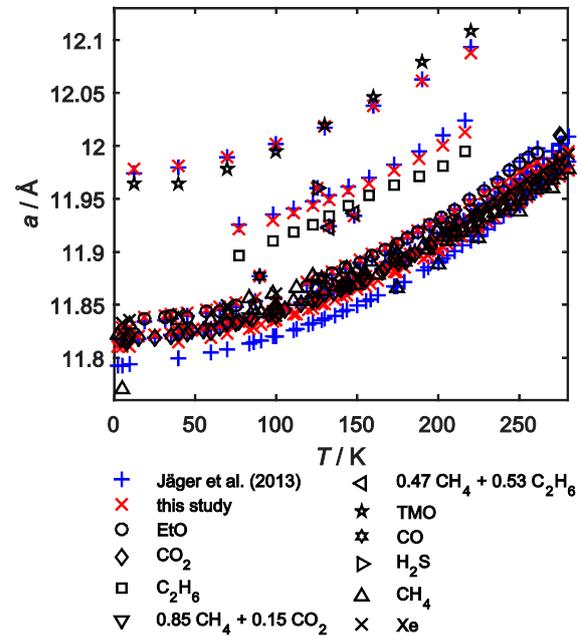

Fig. 1. Experimental data for the temperature dependence of the lattice parameter of sI gas hydrates at low pressures (typically at atmospheric pressure) compared to the correlation by Jäger et al. [1] and the new correlation.
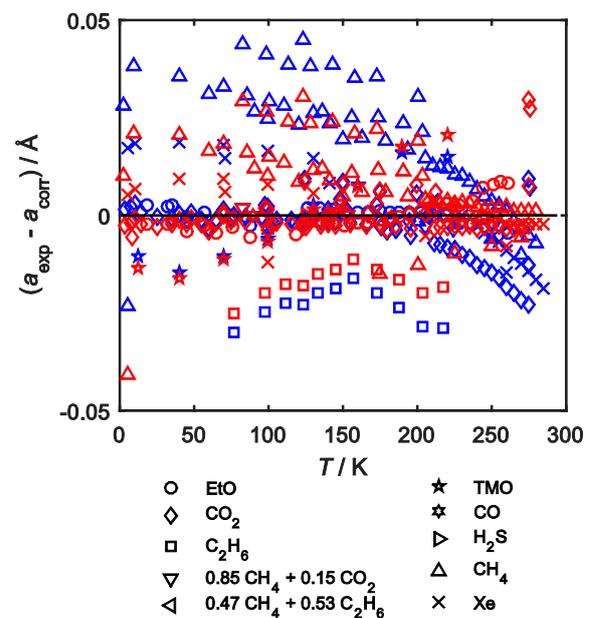

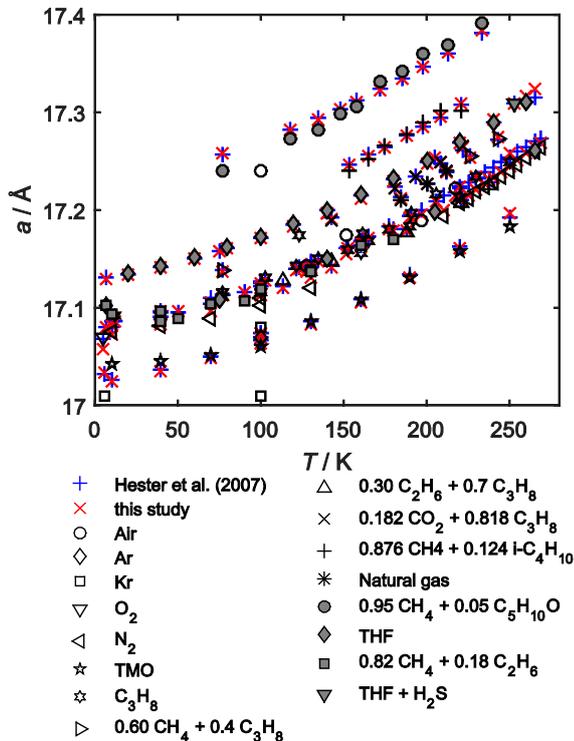**Fig. 2.** Deviation of the correlation by Jäger et al. [13] (blue symbols) and the new correlation (red symbols) from the experimental data for the temperature dependence of the lattice parameter of sI gas hydrates at low pressures (typically at atmospheric pressure).

In the low temperature region below 200 K, both correlations provide relatively good reproduction of the experimental data. Larger deviations can be seen only by some data sets for methane and ethane hydrates caused by slight discrepancies between the temperature data sets and the pressure data sets of these gas hydrates. The new correlation provides significantly better reproduction of the high temperature data for CO_2, CH_4 and Xe hydrates by Hansen et al. [16] from 2016. As already shown in Table 3, the new correlation is in general in better agreement with the experimental data; see Fig. 2.

Fig. 3. Experimental data for the temperature dependence of the lattice parameter of sII gas hydrates at low pressures (typically at atmospheric pressure) compared to the correlation by Hester et al. [17] and the new correlation.

The experimental data for the temperature dependence of the lattice parameter for sII hydrates are compared to the correlation by Hester et al. [17] and the new correlation (12) in Fig. 3. The correlations provide very good reproduction of the experimental data over a wide temperature range. The differences between both correlations are almost negligible in this case, except for the new temperature data for nitrogen hydrates by Hansen et al. [16]. The new correlation is in much better agreement with these data compared to the correlation by Hester et al. [17]. The deviations of both correlations from the experimental data are shown in Fig. 4.

3.3 Results – pressure dependence

The pressure dependence of the lattice parameter for sI hydrates is shown in Fig. 5. The experimental data for four hydrate formers are compared with the correlation employed in the pure hydrate model [3] and with the new correlation (12).

At extremely high pressures above 500 MPa, the results of the new correlation are better for xenon hydrates while slightly worse for ethane hydrates compared to the original correlation [3]. As can be seen in Fig. 6 showing the deviations of both correlations from the experimental data, a noticeable improvement of the new correlation was achieved at pressures below 150 MPa. The new correlation agrees better with the data for methane hydrates and for xenon hydrates in this region.
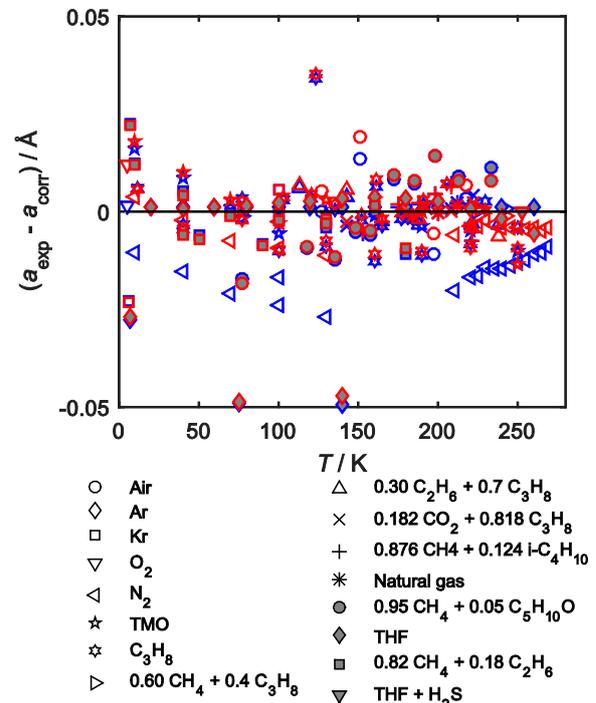

Fig. 4. Deviation of the correlation by Hester et al. [17] (blue symbols) and the new correlation (red symbols) from the experimental data for the temperature dependence of the lattice parameter of sII gas hydrates at low pressures (typically at atmospheric pressure).
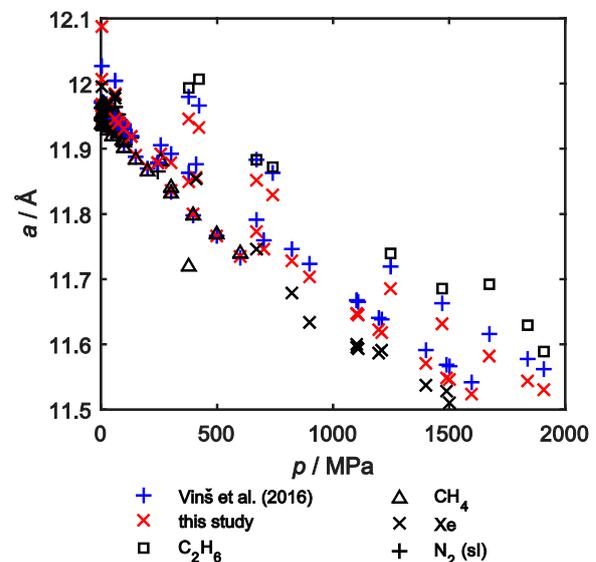

Fig. 5. Experimental data for the pressure dependence of the lattice parameter of sI gas hydrates compared to the correlation by Vinš et al. [3] and the new correlation.
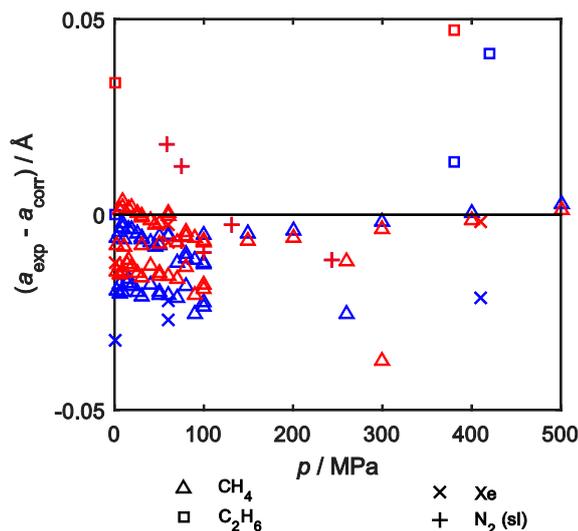
Fig. 6. Deviation of the correlation by Vinš et al. [3] (blue symbols) and the new correlation (red symbols) from the experimental data for the pressure dependence of the lattice parameter of sI gas hydrates.

Fig. 7 shows the pressure dependent data for the lattice parameter of sII hydrates. The two correlations provide comparable results, which are in good agreement with the experimental data in both cases. We note that the data for THF + Xe mixed hydrates up to 3 GPa were considered in this study.
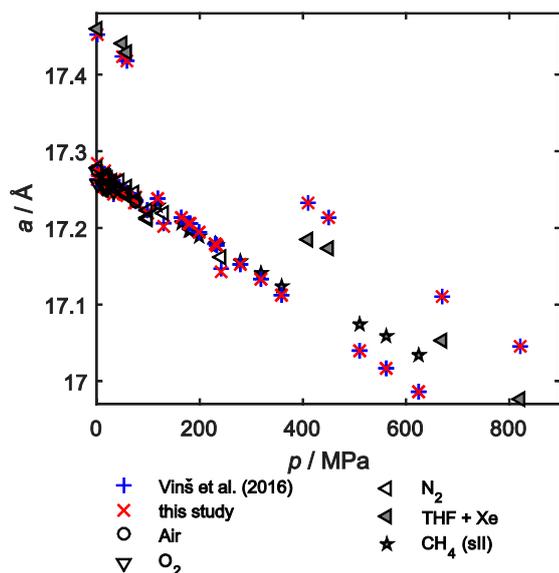

Fig. 7. Experimental data for the pressure dependence of the lattice parameter of sII gas hydrates compared to the correlation by Vinš et al. [3] and the new correlation.

4 Conclusions

The correlation for the temperature and pressure dependences of the lattice parameter of sI and sII gas hydrates developed in the previous study [3] was revised and modified such that it can be used for modeling of mixed hydrates. The new correlation was simultaneously fitted to the experimental data for both the temperature

dependence and the pressure dependence of the hydrate volume using a two-stage Levenberg-Marquardt algorithm. A set of values for the thermal expansion coefficients α_1 to α_3 and for the reference lattice parameter a_0 was evaluated at the reference temperature of 273.15 K and the reference pressure of 1 Pa. The bulk modulus was considered constant and equal to 10 GPa (with $B_0' = 4$) for all selected hydrates.

The new model for the volume of sI and sII gas hydrates is in good agreement with the experimental data, including the recent data of Hansen et al. [16], over wide temperature and pressure ranges. Therefore, the universal modeling approach for sI and sII formers for the temperature dependence of the lattice parameter as proposed by Hester et al. [17] and for the pressure dependence as proposed by Vinš et al. [3] with the new parameters proposed in this work will be used for modeling mixed hydrates.

List of abbreviations

AAD	absolute average deviation
AD	average deviation
Ar	argon
CCS	carbon capture and storage
CH_4	methane
C_2H_6	ethane
C_3H_8	propane
$C_5H_{10}O$	tetrahydropyran
CO	carbon monoxide
CO_2	carbon dioxide
EtO	ethylene oxide
H_2S	hydrogen sulphide
$i\text{-}C_4H_{10}$	isobutane
Kr	krypton
N_2	nitrogen
O_2	oxygen
THF	tetrahydrofuran
TMO	trimethylene oxide
Xe	xenon

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