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# Van't Hoff law for temperature dependent Langmuir constants in clathrate hydrate nanocavities.

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## Abstract

This work gives a van't Hoff law expression of Langmuir constants of different species for determining their occupancy in the nanocavities of clathrate hydrates. The van't Hoff law's parameters are derived from a fit with Langmuir constants calculated using a pairwise site-site interaction potential to model the anisotropic potential environment in the cavities, as a function of temperature. The parameters can be used for calculating clathrates compositions. Results are given for nineteen gas species trapped in the small and large cavities of structure types I and II [1]. The accuracy of this approach is based on a comparison with available experimental data for ethane and cyclopropane clathrate hydrates. The numerical method applied in this work, was recently validated from a comparison with the spherical cell method based on analytical considerations [1]

## 1 Introduction

A clathrate is an ice-like crystalline solid consisting of water molecules forming a cage structure around smaller guest molecules under suitable conditions of low temperature and high pressure. On Earth, it is considered that clathrate hydrates are the most important reservoirs of fossil energy [2, 3], and that favourable conditions for gas hydrate formation exist in about 25% of the earth's land mass. Moreover, the thermodynamics conditions of pressure and temperature prevailing in the oceans are such that hydrates should easily be formed in about 90% of the ocean or sediments. The most common guest molecules in terrestrial clathrates are of organic aliphatic nature like methane, ethane, propane or butane, but other small inorganic molecules like nitrogen, carbon dioxide, and hydrogen sulfide can also be trapped in the cages of clathrates [4, 5, 6, 7, 8, 9, 10]. In the advent of global warming, these clathrates can enhance the temperature rise when the trapped species are released. Clathrate hydrates are also suspected to be extensively present on several planets, satellites and comets of the Solar System. Planetologists are thus concerned with the possible clathrate impact on the distribution of the planet's volatiles and on the modification of their atmosphere's compositions [11]. Hence, it is of great interest to correctly determine

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the amount of species potentially trapped in the cages of clathrates, *i.e.* the fractional occupancy of guest species under the thermodynamic conditions (pressure and temperature) prevailing in the regions where clathrates might form.

From a theoretical point of view, the thermodynamics of the formation or dissociation of clathrates is most often based on the model developed by van der Waals and Platteeuw [12] following the same hypotheses under which was developed the adsorption theory of Langmuir [13]. The Langmuir isotherms of adsorbed molecules on a surface are determined from the calculation of the Langmuir constant, which is also the main parameter to be considered in the determination of the amount of species trapped in the clathrate cages as a function of pressure and temperature.

To calculate these Langmuir constants, most of the models are based on a molecular description of the guest-water interactions using a Lennard-Jones or Kihara potential form. The parameters of these potentials are usually empirically obtained from experimental data of phase equilibrium. Such models most often neglect interactions of the guest molecules with water beyond a few cages only and are therefore questionable [14, 15, 16, 17, 18, 19].

Moreover, it is generally assumed that the environment of the cage in which a gas molecule is trapped in clathrates is of spherical symmetry. Whereas this assumption may be justified for molecules such as  $\text{CH}_4$  or  $\text{NH}_3$ , it is certainly not well-suited for molecules such as  $\text{CO}_2$  and  $\text{N}_2\text{O}$  or  $\text{SO}_2$  which are of cylindrical or oblate symmetry and for which the hypothesis of a free rotation at the center of a spherical cage is no longer valid.

In the case of ethane and cyclo-propane clathrate hydrates, an analytical method based on the spherical cell model has been used to extract spherically averaged intermolecular potentials from experimental data on the temperature dependence of the Langmuir constant by Bazant and Trout [20]. For other guests in clathrate hydrates, in particular, argon, hydrogen, nitrogen, methane, ethane, propane, cyclo-propane, and carbon dioxide, other workers [4, 5, 6, 7, 10] have explicitly taken into account the angle-dependence of the guest-water intermolecular potential in an atom-atom or site-site description to calculate the corresponding Langmuir constants. However, in most of these studies the water and guest molecules were simply described as one, two or three interaction sites for the Lennard-Jones or Kihara potential contributions although more than three sites are involved.

This work aims at providing a van't Hoff law expression of the Langmuir constant for single guest molecules incorporated in clathrate hydrates as a function of the temperature by improving the potential model used in the determination of the Langmuir constants, that is by using an atom-atom and site-site potential and by considering explicitly the effect of water molecules beyond the trapping cage and the resulting anisotropic environment. In the present work, the Langmuir constant is determined by taking into account all the external degrees of freedom of the guest molecules, *i.e.* the center of mass (c.m.) translational motion and the orientational motion in a true crystallographic clathrate lattice, not necessarily of spherical symmetry as it is often assumed when using the van der Waals and Platteeuw model [12]. In the following, we recall in section 2 the model used for the calculations of the Langmuir constants that are necessary to determine the fractional occupancy of guest species in clathrates. Then, in section 3, the geometry and interaction potential considered here are described. Finally, in section 4, the coefficients for a simple van't Hoff expression of the Langmuir constants are given for a large set of guest molecules. The Langmuir constants calculated using this model are compared with available experimental data, *i.e.*, for ethane, cyclo-propane guest molecules.

## 2 Statistical thermodynamic approach

In contrast to natural ice which solidifies in the hexagonal structure, clathrate hydrates form, as water crystallizes, in the cubic system in several different structures which are characterized by specific cages of different sizes. The two most common types are "structure I" and "structure II". In structure I, the unit cell is made of 46 water molecules forming 2 small (12 pentagonal faces  $5^{12}$ ) and 6 large (12 pentagonal and 2 hexagonal faces  $5^{12}6^2$ ) cages, while in structure II, the unit cell is made up of 136 water molecules forming 16 small (12 pentagonal faces  $5^{12}$ ) and 8 large (12 pentagonal and 4 hexagonal faces  $5^{12}6^4$ ) cages

[3].

Calculations of the relative abundances of guest species incorporated in a clathrate lattice structure of type I (sI) or II (sII) at given temperature-pressure conditions can be performed using classical statistical mechanics which allows the macroscopic thermodynamic properties of the clathrates to be determined from the interaction energies between the guest species and the clathrate water molecules.

In 1959 van der Waals and Platteeuw [12] developed a model of clathrate's formation in which the trapping of guest molecules in nano-cages was considered to be a generalized case of the three-dimensional ideal localized adsorption.

Their model is based on the following hypotheses:

1. The contribution of the host molecules to the free energy is independent of the occupational mode in the cages. This implies in particular that the guest species do not distort the trapping cage.
2. The encaged molecules are localized in the cages, each of which can never hold more than one guest.
3. The mutual interaction of the guest molecules is neglected, i.e., the partition function for the motion of a guest molecule in its cage is independent of the other guests.
4. Classical statistics is valid, i.e., quantum effects are negligible.

From the configuration partition function and the thermodynamic equilibrium condition on the chemical potentials of the guest and host molecules in coexisting phases in clathrate [21], the fractional occupancy of a guest molecule  $K$  in a given "structure type-cage size"  $t$  ( $t$  = structure-type I or II-small or large cage) can be written as:

$$y_{K,t} = \frac{C_{K,t}f_K}{1 + \sum_J C_{J,t}f_J}, \quad (1)$$

where the sum in the denominator includes all the species present in the initial gas phase,  $C_{K,t}$  is the Langmuir constant of species  $K$  in the structure type-cage size  $t$ , and  $f_K$  is the fugacity of the species  $K$  which depends on the total pressure  $P$  of the initial gas phase and on the temperature  $T$ .

The Langmuir constant in equation (1) depends on the temperature  $T$  and on the strength of the interaction energy between the guest species  $K$  and the water molecules in the cage. It is expressed as:

$$C_{K,t} = \frac{1}{k_B T} \int \exp\left(-\frac{V_{K,t}(\mathbf{r}, \boldsymbol{\Omega})}{k_B T}\right) d\mathbf{r} d\boldsymbol{\Omega}. \quad (2)$$

In this equation  $V_{K,t}(\mathbf{r}, \boldsymbol{\Omega})$  is the interaction potential energy experienced by the guest molecule for a given position vector  $\mathbf{r}$  of its center of mass with respect to the cage center and its orientational vector  $\boldsymbol{\Omega}$ , and  $k_B$  is the Boltzmann constant. The integral value must be calculated for all external degrees of freedom of the guest molecule inside the structure type-cage size  $t$ .

To evaluate the Langmuir constant  $C_{K,t}$ , two additional assumptions are often made, namely: (i) the symmetry of the guest molecule's environment is considered to be spherical and (ii) the guest molecule can freely rotate in the corresponding spherical cage (spherical cell potential approximation), in accordance with the Lennard-Jones and Devonshire [22] theory applied to liquids.

Then, the Langmuir constant can be cast as:

$$C_{K,t} = \frac{4\pi}{k_B T} \int_0^{R_c} \exp\left(-\frac{V_{K,t}(r)}{k_B T}\right) r^2 dr, \quad (3)$$

where  $R_c$  is the radius of the spherical cage and  $V_{K,t}(r)$  is the spherically averaged potential energy between the guest molecule and the clathrate water molecules.

Note that Eq. (3) is commonly used by planetologists and as a result, it may introduce significant inaccuracies in the evaluation of the relative abundances of gas species in clathrate hydrates when the assumed spherical symmetry of the interaction potential is questionable.

In contrast, the Langmuir constant for enclathrated single guest molecules is determined here by taking into account all the external degrees of freedom of the enclathrated molecules, i.e. the center of mass (c.m.) translational motion and the orientational motion in a real crystallographic clathrate lattice, not necessarily of spherical symmetry. As a consequence, Eq. (3) is no longer valid in our approach and should be replaced by a more general form, as explained below.

### 3 Potential energy model

Let us consider a non-vibrating single gas species (atom or molecule) trapped in a small or large cage of a clathrate structure of type sI or sII. The positions of the hydrogen and oxygen atoms are given by their coordinates in a reference frame fixed to the clathrate lattice, while those of the guest molecule are usually given in a frame tied to the molecule with the  $z$  axis coinciding with the rotational axis of highest symmetry as shown for the trapping of a guest molecule ( $\text{CH}_4$  for instance) in the small cage of the clathrate structure type I, in Figure 1.

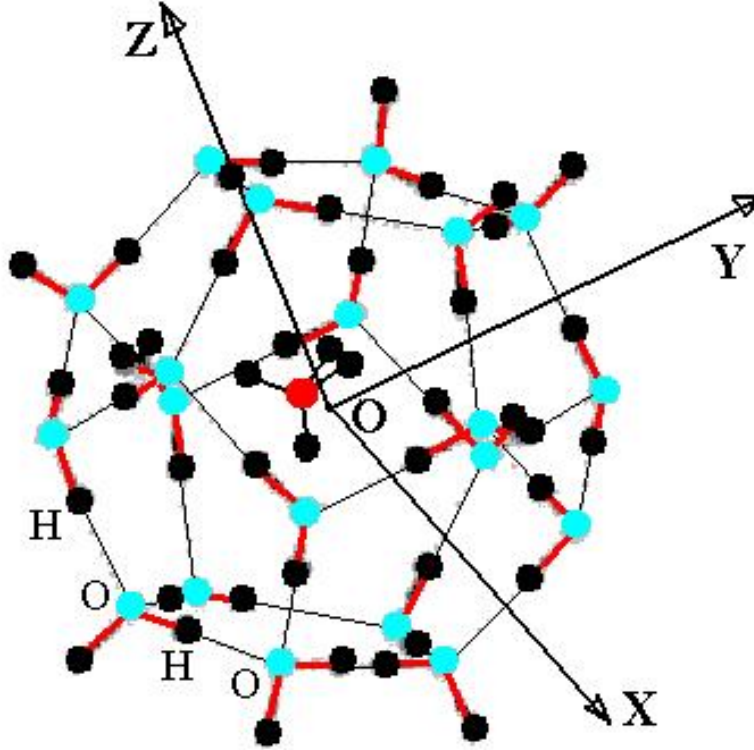


Figure 1: Trapping geometry of a guest molecule ( $\text{CH}_4$  for instance) in a small cage of the structure type I.  $(O, X, Y, Z)$  represents the absolute frame tied to the clathrate lattice.

The interaction potential energy  $V_{K,t}$  between the guest molecule  $K$  and the surrounding water molecules of the structure type-cage size  $t$ , considered as a rigid clathrate crystal, is modeled as a sum of a 12-6 Lennard-Jones (LJ) pairwise atom-atom potential characterizing the repulsion-dispersion con-

tributions and an electrostatic part due to charge-charge interactions between the charges in the guest molecule and those in the water molecules of the clathrate system. It is expressed as:

$$V_{K,t} = \sum_{k=1}^{N_C} \sum_{j=1}^{N_W} \sum_{i=1}^{N_K} \left[ 4\epsilon_{ij} \left\{ \left( \frac{\sigma_{ij}}{|\mathbf{r}_{ij_k}|} \right)^{12} - \left( \frac{\sigma_{ij}}{|\mathbf{r}_{ij_k}|} \right)^6 \right\} + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{|\mathbf{r}_{ij_k}|} \right], \quad (4)$$

where  $\mathbf{r}_{ij_k}$  is the distance vector between the  $i$ th site, with electric charge  $q_i$ , of the guest molecule ( $N_K$  sites) and the  $j$ th site, with electric charge  $q_j$ , of the  $k$ th water molecule ( $N_W$  sites) of the clathrate matrix (containing  $N_C$  water molecules);  $\epsilon_{ij}$  and  $\sigma_{ij}$  are the mixed LJ potential parameters, using the Lorentz-Berthelot combination rules as:

$$\epsilon_{ij} = \sqrt{\epsilon_i \epsilon_j} \quad \text{and} \quad \sigma_{ij} = \frac{\sigma_i + \sigma_j}{2}, \quad (5)$$

where  $\epsilon_i$  and  $\sigma_i$  are the Lennard-Jones parameters for the  $i - i$  interacting atomic pair, which are taken from the literature [23, 24, 26]. The effective electric charges for the water molecules  $q_H = +0.4238 e$ ,  $q_O = -0.8476 e$  are from reference [25] and those for the guest species are from references [25, 26, 27, 28, 29].

Table 1: Pure Lennard-Jones potential parameters<sup>(a)</sup> used in our calculations.

	H - H	O - O	C - C	N - N	S - S	Ne - Ne	Ar - Ar	Kr - Kr	Xe - Xe
$\epsilon_i$ (K)	8.59	57.41	42.88	37.29	73.79	43.16	126.90	179.85	226.03
$\sigma_i$ (Å)	2.810	3.030	3.210	3.310	3.390	2.764	3.405	3.650	3.970

(a) Obtained from Refs. [23, 24, 26].

Calculations of the Langmuir constant  $C_{K,t}$  from Eq. (2) require an explicit determination of the external degrees of freedom of the guest molecule, that is, its center of mass (c.m.) position vector  $\mathbf{r}$  and its orientation vector  $\boldsymbol{\Omega} = (\varphi, \theta, \chi)$ . Therefore, we define an absolute frame (O,  $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$ ) connected to the clathrate matrix.

Figure 2 gives the geometrical characteristics of the guest-water interacting molecules, and a description of the internal positions of the sites in the guest molecule with respect to its frame (G,  $\mathbf{x}, \mathbf{y}, \mathbf{z}$ ) and its external orientational and translational degrees of freedom with respect to the absolute frame (O,  $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$ ).

Then, the distance vector  $\mathbf{r}_{ij_k}$  in Eq. (4) can be expressed in terms of the position vector  $\mathbf{r}$  of the c.m. of the guest molecule and  $\mathbf{r}_{j_k}$  of the  $j$ th site of the  $k$ th water molecule with respect to the absolute frame (O,  $\mathbf{X}, \mathbf{Y}, \mathbf{Z}$ ), and of the position vector  $\eta_i$  of the  $i$ th site of the guest molecule with respect to its associated frame (G,  $\mathbf{x}, \mathbf{y}, \mathbf{z}$ ) (see Figure 2), as:

$$\mathbf{r}_{ij_k} = \mathbf{r}_{j_k} - \mathbf{r} - \eta_i. \quad (6)$$

It should be noted that the explicit dependence upon the angular degrees of freedom  $\varphi$ ,  $\theta$ , and  $\chi$  of the guest molecule requires the determination of the site position vectors  $\{\eta\}$  with respect to the absolute frame.

Then, by assuming (i) that the guest species and water molecules are rigid, and (ii) that the clathrate lattice is undistorted (static lattice), the Langmuir constant is calculated from a six-dimensional configurational integral written as:

$$C_{K,t} = \frac{1}{k_B T} \int \exp \left( - \frac{V_{K,t}(x, y, z, \varphi, \theta, \chi)}{k_B T} \right) dx dy dz d\varphi \sin \theta d\theta d\chi. \quad (7)$$

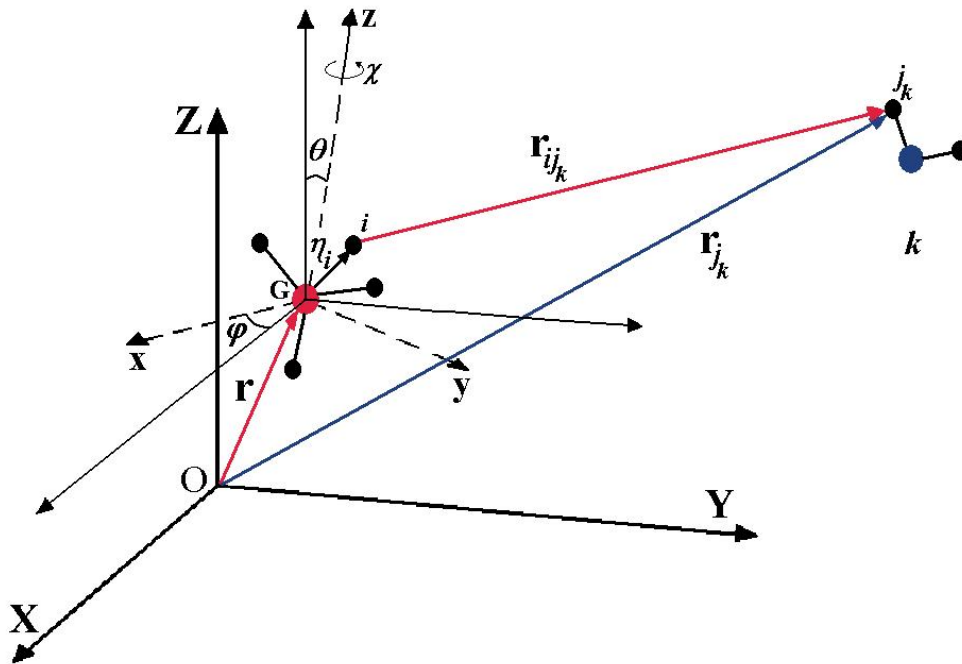


Figure 2: Geometrical characteristics of a guest molecule ( $\text{CH}_4$  for instance) interacting with a water molecule of the clathrate matrix.  $(O, X, Y, Z)$  and  $(G, x, y, z)$  represent the absolute frame tied to the clathrate matrix and the molecular frame, respectively.

Of course, it should be noted that (i) for atomic species, there are no orientational variables, and (ii) for linear molecules there is no spinning variable  $\chi$ .

## 4 Results and discussion

As already described above, we herein use a pairwise atom-atom Lennard-Jones and a site-site electrostatic potentials for calculating the interaction of single guest molecules with clathrate matrices containing  $4 \times 4 \times 4$  unit cells (up to 2944 water molecules) for the structure sI, and  $3 \times 3 \times 3$  unit cells (up to 3672 water molecules) for the structure sII. Indeed, it has been previously shown that these number of water molecules are large enough to ensure a good convergence of the corresponding calculations [30]. Moreover, in order to determine the Langmuir constant and its temperature dependence for a guest molecule  $K$

in a structure type-cage size  $t$  of clathrate, the potential energy surface  $V_{K,t}(x, y, z, \varphi, \theta, \chi)$  in Eq. (7) is first numerically computed for all the center of mass positions and orientations of the molecule with respect to the absolute frame as defined, and then the numerical integration is performed. Note that the minimum of the potential energy  $V_{K,t}^{\min}$  and the associated molecular position and orientation can also be determined in this way.

#### 4.1 Calculation and fit of the Langmuir constants

A clathrate is characterized by its degree of occupancy *i.e.* the fraction of cage sites that is occupied by a guest molecule, which can be calculated from the knowledge of the Langmuir constant  $C_{K,t}$ . Because such constants are not necessarily extracted from experiments in a large range of temperatures, we propose here to express them as a function of temperature through a simple van't Hoff law :

$$C_{K,t}(T) = A_{K,t} \exp(B_{K,t}/T), \quad (8)$$

in which  $A$  ( $\text{Pa}^{-1}$ ) and  $B$  (K) are constant values fitted to values derived from an atomic description of the clathrate systems. This simple van't Hoff expression could thus be readily used, for instance, by planetologists in the large range of temperatures encountered in the Solar System.

In this work Langmuir constants have been calculated for eighteen species, in the temperature range between 50 K and 300 K, as given in Tables 2, 3 and 4 for rare gas atoms, linear molecules and non-linear molecules, respectively.

Table 2: Parameters  $A_{K,t}$  ( $\text{Pa}^{-1}$ ) and  $B_{K,t}$  (K) for the van't Hoff expression of the Langmuir constant for simple guest clathrate hydrates.

Structure type Cage size	sI small cage	sI large cage	sII small cage	sII large cage
Guest species $K$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$
Ne	$1.0308 \times 10^{-9}$ 1187.948	$2.7194 \times 10^{-9}$ 1015.862	$0.8154 \times 10^{-9}$ 1233.898	$5.6151 \times 10^{-9}$ 898.062
Ar	$1.5210 \times 10^{-10}$ 2961.545	$7.7829 \times 10^{-10}$ 2521.758	$1.0456 \times 10^{-10}$ 2977.025	$2.4531 \times 10^{-10}$ 2195.964
Kr	$0.5985 \times 10^{-10}$ 3885.383	$3.8799 \times 10^{-10}$ 3454.028	$0.4004 \times 10^{-10}$ 3789.957	$16.2508 \times 10^{-10}$ 3021.690
Xe	$1.9389 \times 10^{-11}$ 4547.654	$13.8509 \times 10^{-11}$ 4572.732	$1.2913 \times 10^{-11}$ 4085.506	$83.2357 \times 10^{-11}$ 4103.672



Table 3: Parameters  $A_{K,t}$  ( $\text{Pa}^{-1}$ ) and  $B_{K,t}$  (K) for the van't Hoff expression of the Langmuir constant for simple guest clathrate hydrates.

Structure type Cage size	sI small cage	sI large cage	sII small cage	sII large cage
Guest species $K$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$
H <sub>2</sub>	$4.7301 \times 10^{-9}$ 1265.757	$16.0695 \times 10^{-9}$ 1515.721	$5.5295 \times 10^{-9}$ 1203.620	$64.0074 \times 10^{-9}$ 873.259
O <sub>2</sub>	$1.3153 \times 10^{-9}$ 2917.693	$7.4606 \times 10^{-9}$ 2558.746	$0.8004 \times 10^{-9}$ 3044.536	$25.8421 \times 10^{-9}$ 2238.052
N <sub>2</sub>	$3.9496 \times 10^{-10}$ 2869.400	$25.6897 \times 10^{-10}$ 2680.372	$4.8836 \times 10^{-10}$ 2679.423	$201.3238 \times 10^{-10}$ 2226.480
CO	$2.5937 \times 10^{-10}$ 3518.021	$16.5331 \times 10^{-10}$ 3075.059	$4.5198 \times 10^{-10}$ 3088.930	$229.8631 \times 10^{-10}$ 2275.803
CO <sub>2</sub>	$7.7765 \times 10^{-12}$ 2976.629	$520.5579 \times 10^{-12}$ 4674.690	$7.9970 \times 10^{-12}$ 2277.757	$6907.0012 \times 10^{-12}$ 3370.363
HCN	$7.6653 \times 10^{-12}$ 4085.369	$131.1607 \times 10^{-12}$ 4328.556	$13.9141 \times 10^{-12}$ 2593.031	$8224.5133 \times 10^{-12}$ 2640.868
C <sub>2</sub> H <sub>2</sub>	$0.9702 \times 10^{-12}$ 735.205	$221.9622 \times 10^{-12}$ 3076.356	$0.2439 \times 10^{-12}$ 321.114	$3909.8421 \times 10^{-12}$ 2837.467

## 4.2 Comparison with available experimental Langmuir constants

### 4.2.1 Ethane and cyclo-propane simple hydrates

In Tables 5 and 6, the Langmuir constants calculated here are compared to experimental values obtained from the dissociation pressure data by Sparks and Tester [4] for temperatures ranging between 200 K and 290 K and between 240 K and 290 K, for ethane and cyclo-propane trapped in large cages of structure sI, respectively. Moreover, for comparison the Langmuir constants calculated from a simple spherical model as often used in the literature are also reported in Tables 5 and 6.

It can be seen that the values calculated here are in good agreement with those extracted from experimental data. The ratios  $C_{\text{cal}}/C_{\text{exp}}$  vary between 0.5 and 1.2 for ethane, and between 0.7 and 1.1 for cyclo-propane, depending on temperature. Note that the same ratios calculated within the same temperature range for the large cages of structure sII lead to values ranging from 320 to 540 for ethane, and from 920 to 1100 for cyclo-propane. These results are consistent with the fact that ethane and cyclo-propane form sI-large cage clathrate hydrates only. Moreover, Tables 5 and 6 show that the best agreement between the values calculated here and those extracted from experiments is found when temperature is higher than 260 K. Below this temperature, the calculated values are systematically lower than the

Table 4: Parameters  $A_{K,t}$  ( $\text{Pa}^{-1}$ ) and  $B_{K,t}$  (K) for the van't Hoff expression of the Langmuir constant for simple guest clathrate hydrates.

Structure type Cage size	sI small cage	sI large cage	sII small cage	sII large cage
Guest species $K$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$	$A_{K,t}$ $B_{K,t}$
H <sub>2</sub> S	$2.3444 \times 10^{-10}$ 4463.910	$7.2080 \times 10^{-10}$ 4073.045	$3.6415 \times 10^{-10}$ 3073.324	$758.3575 \times 10^{-10}$ 2495.937
SO <sub>2</sub>	$1.2311 \times 10^{-12}$ 4374.084	$75.0641 \times 10^{-12}$ 6272.810	$6.1515 \times 10^{-12}$ 1548.504	$17926.7530 \times 10^{-12}$ 4139.948
NH <sub>3</sub>	$8.6697 \times 10^{-11}$ 5197.361	$27.5220 \times 10^{-11}$ 4975.753	$38.7320 \times 10^{-11}$ 3334.132	$5031.4000 \times 10^{-11}$ 2484.181
CH <sub>4</sub>	$8.3453 \times 10^{-10}$ 2901.747	$116.6313 \times 10^{-10}$ 2959.901	$5.4792 \times 10^{-10}$ 2546.660	$829.8039 \times 10^{-10}$ 2629.194
C <sub>2</sub> H <sub>6</sub> <sup>(a)</sup>	- -	$3.5164 \times 10^{-11}$ 4226.997	- -	$727.2717 \times 10^{-11}$ 4440.484
cyc-C <sub>3</sub> H <sub>6</sub> <sup>(a)</sup>	- -	$1.4881 \times 10^{-11}$ 4781.938	- -	$402.4295 \times 10^{-11}$ 5161.620
C <sub>3</sub> H <sub>8</sub> <sup>(a)</sup>	- -	$5.5707 \times 10^{-13}$ 3537.025	- -	$597.9850 \times 10^{-13}$ 7118.782
iso-C <sub>4</sub> H <sub>10</sub> <sup>(a)</sup>	- -	$2.7970 \times 10^{-14}$ 1598.004	- -	$208.3210 \times 10^{-14}$ 7103.169

(a) When the potential energy surfaces are positive, the Langmuir constants are negligible and the parameters  $A_{K,t}$  and  $B_{K,t}$  are not given.

experimental ones.

To extract a quantitative value for our comparison, we use the following least square deviation parameter  $\sigma$  defined as:

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (C_{\text{cal}} - C_Y)^2}{N - 1}}, \quad (9)$$

where  $C_{\text{cal}}$  are the values calculated at different temperatures in this work and  $C_Y$  are the values obtained experimentally [4] or from the spherical model as often used in the literature.  $N$  is the number of temperatures considered ( $N = 10$  in Table 5). We find values of  $\sigma$  equal to  $1.6 \times 10^{-2} \text{ Pa}^{-1}$  and 3.3

Table 5: Calculated and experimental Langmuir constants ( $\text{Pa}^{-1}$ ) for ethane trapped in large cage of structure sI. Experimental values are obtained from reference [4].

$T$ (K)	$C_{\text{cal. this work}}$	$C_{\text{exp.}}$	$C_{\text{cal. Spherical model}}$
200	$5.3 \times 10^{-2}$	$9.9 \times 10^{-2}$	$14.7 \times 10^{-2}$
210	$2.0 \times 10^{-2}$	$3.2 \times 10^{-2}$	$5.2 \times 10^{-2}$
220	$7.8 \times 10^{-3}$	$12.0 \times 10^{-3}$	$20.2 \times 10^{-3}$
230	$3.4 \times 10^{-3}$	$4.6 \times 10^{-3}$	$8.5 \times 10^{-3}$
240	$1.6 \times 10^{-3}$	$1.9 \times 10^{-3}$	$3.9 \times 10^{-3}$
250	$7.7 \times 10^{-4}$	$8.4 \times 10^{-4}$	$18.6 \times 10^{-4}$
260	$4.0 \times 10^{-4}$	$4.1 \times 10^{-4}$	$9.5 \times 10^{-4}$
270	$2.2 \times 10^{-4}$	$2.0 \times 10^{-4}$	$5.1 \times 10^{-4}$
280	$1.3 \times 10^{-4}$	$1.1 \times 10^{-4}$	$2.9 \times 10^{-4}$
290	$7.5 \times 10^{-5}$	$6.1 \times 10^{-5}$	$16.7 \times 10^{-5}$

Table 6: Calculated and experimental Langmuir constants ( $\text{Pa}^{-1}$ ) for cyclo-propane trapped in large cage of the sI structure. Experimental values are obtained from reference [4].

$T$ (K)	$C_{\text{cal. this work}}$	$C_{\text{exp.}}$	$C_{\text{cal. Spherical model}}$
240	$6.7 \times 10^{-3}$	$9.5 \times 10^{-3}$	$0.12 \times 10^{-3}$
250	$3.0 \times 10^{-3}$	$3.8 \times 10^{-3}$	$0.06 \times 10^{-3}$
260	$1.5 \times 10^{-3}$	$1.7 \times 10^{-3}$	$0.04 \times 10^{-3}$
270	$7.3 \times 10^{-4}$	$7.6 \times 10^{-4}$	$0.23 \times 10^{-4}$
280	$3.9 \times 10^{-4}$	$3.8 \times 10^{-4}$	$0.15 \times 10^{-4}$
290	$2.2 \times 10^{-4}$	$2.0 \times 10^{-4}$	$0.10 \times 10^{-4}$

$\times 10^{-2} \text{ Pa}^{-1}$ , respectively. Moreover, note that in our calculations, the minimum of the potential energy corresponds to ethane's center of mass located at  $0.12 \text{ \AA}$  from the center of the large cage of structure sI, i.e., a value that is consistent with observations from single crystal X-ray diffraction studies that place the center of mass at  $0.17 \text{ \AA}$  from the center of the large cage [31].

As for cyclo-propane (values given in Table 6 ( $N = 6$ )), we calculate values of  $\sigma$  equal to  $1.3 \times 10^{-3} \text{ Pa}^{-1}$  and  $3.3 \times 10^{-3} \text{ Pa}^{-1}$ , respectively.

To summarize, when compared to experimental results, the values of the Langmuir constants calculated here for ethane show a better agreement with experimental data than those calculated from the spherical model, although they are of the same order of magnitude.

Nevertheless, for cyclo-propane Table 6 shows that values obtained from a simple spherical model disagree with experimental data and then they are certainly not correct.

Therefore, the comparison of values calculated in this work with values issued from experimental work provides firm and sufficient grounds to validate the results obtained here for ethane and cyclo-propane.

## 5 Conclusions

In the present work, calculations of the Langmuir constants and their temperature dependence for simplest clathrate hydrates have been performed for nineteen gas species using the van der Waals and Platteeuw model and an all-atom approach for calculating the interactions between guest and water molecules in the clathrate cages. This approach accounts for the atomic character of the guest species and for the non-spherical water environment.

Then, the temperature dependence of the Langmuir constants in the range  $50 \text{ K} - 300 \text{ K}$  is given in the form of a van't Hoff expression with parameters obtained from a fit to calculated values.

This simple expression could thus be easily applied in various situations, especially when experimental data are not available. For example, it can help planetologists in the determination of the fractional occupancies of gas species trapped in the clathrates that are suspected to exist in various solid bodies of the Solar System. Indeed, this information is mandatory to analyze the atmospheric compositions of planets and satellites like Mars and Titan, for example, and thus to better understand their way of formation. Unfortunately, the temperatures usually considered in clathrate experiments are often far from the temperature range of interest for Planetology. As a consequence, calculations of clathrate occupancies is a preliminary step for any formation scenario that would consider clathrate influence. In that purpose, using the van't Hoff expression given here would be much more simple than the usual approaches.

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