



# A simple van't Hoff law for calculating Langmuir constants in clathrate hydrates



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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 clathrate hydrates. First, a pairwise site–site interaction potential energy model is used to calculate the Langmuir constants in an otherwise anisotropic potential environment, as a function of temperature. The results are then fitted to a van't Hoff law expression to give a set of parameters that can be used for calculating clathrates compositions. The van't Hoff law's parameters are given for eighteen gas species trapped in the small and large cavities of structure types I and II. The accuracy of this approach is based on a detailed comparison with available experimental and/or previously calculated data for ethane, cyclo-propane, methane and carbon dioxide clathrate hydrates. A comparison with the analytical cell method is also carried out to better understand the importance of asymmetry and possible limitations of the van't Hoff temperature dependence.

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## 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 [1,2], and that favorable 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 [3–9]. 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 [10]. Hence, it is of

great interest to correctly determine 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 [11] following the same hypotheses under which was developed the adsorption theory of Langmuir [12]. 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 [13–18].

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 CH<sub>4</sub> or NH<sub>3</sub>, it is certainly not well-suited for

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molecules such as CO<sub>2</sub> and N<sub>2</sub>O or SO<sub>2</sub> 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 [19]. The cell potential method has then been extended to other molecules like methane, propane, isobutane and small chlorofluorocarbon molecules, showing a good accuracy in reproducing both dissociation pressures and phase diagrams of hydrocarbon mixtures [7,8]. This method thus appears as a very interesting and quite simple approach for predictions of clathrate hydrate equilibrium properties. However, it should be mentioned that, for some cases, the central-well potential does not satisfactorily reproduce the shape of the guest–water potential at the center of the clathrate cages. Although Anderson et al. [8] claimed that this has no influence on the accuracy of the Langmuir constants calculated for Argon, the influence of this failure should be carefully analyzed each time it is evidenced. For other guests in clathrate hydrates, in particular, argon, hydrogen, nitrogen, methane, ethane, propane, cyclo-propane, and carbon dioxide, other workers [3–6,9] 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 [19] 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 as discussed in reference [10], 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 [11]. 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 and/or calculated data, *i.e.*, for ethane, cyclo-propane, methane and carbon dioxide 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<sup>12</sup>) and 6 large (12 pentagonal and 2 hexagonal faces 5<sup>12</sup>6<sup>2</sup>) cages, while in structure II, the unit cell is made up of 136 water molecules forming 16 small (12 pentagonal faces 5<sup>12</sup>) and 8 large (12 pentagonal and 4 hexagonal faces 5<sup>12</sup>6<sup>4</sup>) cages [2].

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 [11] 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 [20], 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 Eq. (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 [21,22] 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

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