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# HOW TO EXPLAIN THE HYDRATE COMPOSITION FROM CO2-C1-C2 GAS MIXTURES: TOWARD A KINETIC UNDERSTANDING VERSUS THERMODYNAMIC AND CONSEQUENCES ON THE EVALUATION OF THE KIHARA PARAMETERS.

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**ABSTRACT**

This work is a contribution to the global understanding of the coupling between kinetic and thermodynamic to explain the clathrate hydrates composition during their crystallization from a water liquid phase and a hydrocarbon gas phase. We faced new experimental facts that opened questioning after comparing the classical modeling of clathrate hydrates following the approach of van der Waals and Platteeuw with our experimental data following a new procedure allowing determining the hydrate composition during crystallization and at equilibrium. In our kinetic model (Herri et al, 2012), the enclathratation is described by means of a Langmuir absorption where the composition if fixed from kinetic consideration based on the balance between the absorption rate and desorption rate. These rates turn out to become dependent on the gas diffusion around the hydrate crystals, and so, the geometry of the system needs to be taken into account, especially the mass transfer at the Gas/liquid interface. The procedure results in the definition of non-equilibrium hydrate compositions with a new analytical expression for this composition.

In this work, our contribution is to extract self-coherent experimental results from literature,, and to re-evaluate properly the Kihara parameters. This step implies to compile and implement all the literature data in a data base of a modeling program (called GasHyDyn in our study). Then, we can optimize Kihara parameters from a procedure that can be trivial in some cases where literature data are rich enough to optimize directly the parameters. Then, from the comparison of experimental results (Bouillot et al., 2014, ICGH8) to the model (this work), we conclude that the experimental protocol can affect the composition of the hydrates, especially if the crystallization is operated near, or far from thermodynamic equilibrium.

*Keywords*: thermodynamics, kinetics, fundamentals, hydrate composition.

## INTRODUCTION

The van der Waals and Platteeuw model (1959) describes the hydrate phase by means of statistical thermodynamics, which allows the description of the different parameters of the system and links them to quantities like temperature, volume and chemical potential. This model has been used for decades. It is a reference model, from which we can compare experimental data, once we assume that it has been correctly fitted.

In this work, we come back to a brief description of the thermodynamic model (more detailed in Sloan, 1998). Then, we focus on the adsorption step. In the end, we go further in the interpretation of the model. In fact, the experimental equilibria might be a consequence of a kinetic process (Herri and Kwaterski, 2012). It opens a discussion on the consequences of non equilibrium crystallization where the gas hydrates compositions can be different from thermodynamic modeling predictions, only because of kinetic limitations such as the mass transfer limitations at the interfaces, or growth limiting rates.

In details, in this paper:

- we recall the fundamental of thermodynamics of gas hydrates,

- we come back to the details of the Langmuir adsorption rule to emphasize that the adsorption is a kinetic mechanism,
- taking into account the non equilibrium adsorption of gas in a gas hydrate solid under growing, we give the fundamentals to model the hydrate composition during crystallization,
- we come back to the thermodynamic modeling of CO2-C1-C2 gas hydrates: and we choice experimental data to fit, being sure that the selected data are at thermodynamic equilibrium:
- we present two sets of experimental data, performed in similar conditions except that one is high rate, and the other one low rate of crystallization. We show that the low rate crystallization tends to be form equilibrium hydrates, and the high rate of crystallization forms hydrates which are clearly not at equilibrium.

## THERMODYNAMIC MODELING

In the case of hydrates, the thermodynamic equilibrium is the equality of chemical potentials of water in the liquid phase and in the hydrate phase. This relationship can be rewritten by introducing reference states. For the hydrate, the reference state used in the van der Waals and Platteeuw model is a hypothetical phase β which corresponds to the empty cavities. The equilibrium equation is then

$$\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta} = \Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta} \qquad (1)$$

Where $\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta}$ and $\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta}$ are the differences of the chemical potentials between water in hydrate or liquid phase and water in the reference state, respectively. $\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta}$ is then determined from statistical thermodynamics, whereas $\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta}$ is determined by means of relations from classical thermodynamics.

### Modeling of $\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta}$

$$\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta} = RT\sum_i \nu_i \ln\left(1-\sum_j \theta_j^i\right) \qquad (2)$$

In Eq.(2) $\nu_i$ is the number of cavities of type $i$ per mole of water (see table 1) and $\theta_j^i$ is the occupancy factor ($\theta_j^i \in [0,1]$) of the cavities of type $i$ by the gas molecule $j$. This last parameter is very important to define the thermodynamic equilibrium and to determine the hydrate properties.

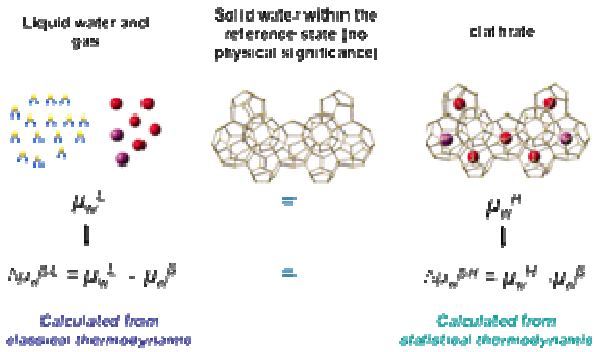


Figure 1 : Schematic of the equilibrium between the clathrate hydrate phase and the liquid phase using a reference state.

### Modeling of $\Delta\mu_w^{\varphi-\beta}$

The chemical potential of water in the aqueous phase is calculated by means of the Gibbs-Duhem equation of classical thermodynamics which expresses the variation of the free enthalpy with temperature, pressure and composition. The reference conditions are the temperature $T_0 = 273.15$ K and the pressure $P_0 = 1$ bar. The difference of the chemical potential of water between the reference phase (liquid in our case, but it could be ice or vapour phase) and the (hypothetical) empty hydrate phase $\beta$, $\Delta\mu_w^{\varphi-\beta}$, can be written as follows:

$$\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta} = T\frac{\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta}\big|_{T^0,P^0}}{T^0} - T\int_{T^0}^{T}\frac{\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\big|_{P^0}}{T^2}dT + \int_{P^0}^{P}\Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\big|_T dP - RT\ln a_{\mathrm{w}}^{\mathrm{L}}\big|_{T,P} \qquad (3)$$

The activity of water in the liquid phase, $a_{\mathrm{w}}^{\mathrm{L}}$, is given as the product of the mole fraction of water in the liquid phase, $x_{\mathrm{w}}$, and the activity coefficient of water, $\gamma_{\mathrm{w}}^{\mathrm{L}}$, hence $a_{\mathrm{w}}^{\mathrm{L}} = x_{\mathrm{w}}\gamma_{\mathrm{w}}^{\mathrm{L}}$. In a good approximation, the aqueous phase (this work) can be regarded as ideal and the activity coefficient therefore can be set to unity, resulting in

$a_{\mathrm{w}}^{\mathrm{L}} \cong x_{\mathrm{w}}$ . However, in the presence of polar molecules, or salts, the system usually shows strong deviations from ideality and $\gamma_{\mathrm{w}}^{\mathrm{L}}$ needs an appropriate description, for example using eNTRL model (Kwaterski and Herri, 2014).

The value of $\Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T}$ is a first order parameter. It has been measured with high accuracy by von Stackelberg (1951) from X ray diffraction. Since that data is believed to be very reliable, the parameter $\Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T}$ in our model calculations has been taken from this source.

The value of $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{P^0}$ is a first order parameter as well. A refinement of the model is given by Sloan (1998, 2007) that takes into account the temperature dependence of $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{P^0}$ using the well-known classical thermodynamic relationship

$$\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{P^0} = \Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T^0,\,P^0} + \int_{T^0}^{T} \Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{P^0} dT \qquad (4)$$

assuming a linear dependence of $\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{P^0}$ on temperature according to:

$$\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{P^0} = \Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T^0,P^0} + b_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\left(T - T^0\right) \qquad (5)$$

The model becomes first order dependent on $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T^0,P^0}$ (hereafter referred as $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta,0}$ ) and second order dependent on $\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T^0,P^0}$ (hereafter abbreviated as $\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta,0}$) and $b_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}$.

The last first order parameter of the equation is $\Delta \mu_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T^0,P^0}$ (hereafter referred to as $\Delta \mu_{\mathrm{w}}^{\mathrm{L}-\beta,0}$)

The values of $\Delta \mu_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T^0,P^0}$ (here after called $\Delta \mu_{\mathrm{w}}^{\mathrm{L}-\beta,0}$), $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta,0}$ , $\Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_{T}$ , $\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta,0}$ and $b_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}$ have been detailed by Sloan (1998). A special attention has been given by us to the values of $\Delta \mu_{\mathrm{w}}^{\mathrm{L}-\beta,0}$ *and* $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta,0}$ because Sloan (1998) has reported different values from different authors, and he retained the data from Dharmawardhana et al (1980). From our work (Herri et al, 2011), from fitting from experimental data about the CO2-N2-CH4 hydrate equilibrium, we prefer now to work with the values from Handa and Tse (1986), given in Herri et al (2011).

## LANGMUIR APPROACH DESCRING THE ENCLATHRATION DURING CRYSTALLIZATION FROM KINETIC CONSIDERATIONS

The classical approach of van der Waals and Platteeuw (1959) provides a description of the thermodynamics of equilibrium involving clathrate hydrate phases. In this approach, the encapsulation of gas molecules in the empty cavities is described similarly to the adsorption of molecules on a two dimensional surface. The model assumptions lead to a Langmuir type of equation for describing this “adsorption” of guest species onto the empty lattice sites.

The simplest case considered deals with a hydrate system containing a single type of guest species $j = j_0$ and a single type of cavity $i = i_0$ . In the second case, hydrate formation in a system containing $N_{\mathrm{g}}$ different potential guest species $j = 1,...,N_{\mathrm{g}}$ in a single type of cavity $i = i_0$ is taken into account. The third case treated here generalises the second case by taking into account the presence of $N_{\mathrm{cav}}$ different types of cavities $i = 1,...,N_{\mathrm{cav}}$ in the empty, metastable hydrate lattice. In the following, the set of indices of the guest components, $\{1,...,N_{\mathrm{g}}\}$ , is designated as $S_{\mathrm{g}}$ , whereas the set $\{1,...,N_{\mathrm{cav}}\}$ counting these indices $i$ is denoted as $S_{\mathrm{cav}}$ .

During crystallisation (here in a liquid system), the crystal is assumed to be surrounded by two successive layers: an integration layer and a diffusion layer. The integration layer is the region of volume in which a transition between the solid state and the liquid state occurs. Following the approach of Svandal et al. (2006), the integration layer can be considered as a solidification layer. It is

described by means of the scalar phase field and a variable composition. The composition of the liquid phase layers with respect to $j = 1, ..., N_g$ species is characterized by a vector of generalized concentrations $\vec{\zeta} = (\zeta_1, \ldots, \zeta_{N_g})^T$. For chemical engineering applications, especially crystallisation processes in liquids, liquid phase non-idealities are often neglected and the fugacity is replaced by a concentration variable $\zeta_j$. In this section, and in the remaining parts of this work, the variable is chosen to be the mole fraction $x$. At the interface between the solid and the integration layer, the scalar phase field assumes the value 1 (solid state). Furthermore, local equilibrium is assumed. The local equilibrium composition is characterized by the set of mole fractions $x_j$ for all $j \in S_g$. Then, in the direction of the second interface, between the integration layer and the diffusion layer, the scalar field varies from 1 (solid state) to 0 (liquid state), and the composition varies from $x_j$ to $x_{j,\mathrm{int}}$. In contrast to Svandal et al. (2006), a model description of the profiles of the scalar phase field or the composition variables is not given in this work. We only assume that they exist (Herri and Kwaterski, 2012). The modelling of the diffusion layer is easier, since it is a liquid, though continuous, phase throughout. The composition varies from $x_{j,\mathrm{int}}$ at the interface between the integration layer and the diffusion layer to $x_{j,\mathrm{bulk}}$ at the interface between the diffusion layer and the liquid bulk phase. A schematic representation of the different regions surrounding the hydrate phase under formation conditions is given in Figure 2.

In such a system, the different species $j$ are enclosed by the sites in proportion to their relative affinity. The rate of enclathratation, $r_{ji,\mathrm{e}}$, is directly proportional to the product of the mole fraction $x_{j,\mathrm{int}}$ of $j$ and the fraction of empty cavities, $1-\theta_i$, according to

$$r_{ji,\mathrm{e}} = k_{x,\,ji,\mathrm{e}} x_{j,\mathrm{int}} (1-\theta_i), \tag{6}$$

where $k_{x,\,ji,\mathrm{e}}$ is the corresponding kinetic rate constant of enclathration of species $j$ in a cavity of type $i$,. The subscript $x$ at the symbol $k$ refers to the mole fraction as the particular concentration variable chosen for $\zeta$.

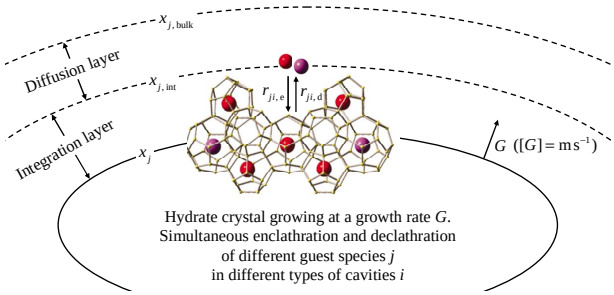


Figure 2. Elementary steps of gas integration in the vicinity of the growing hydrate surface.

The liberation of guest species $j$ from the cavities of type $i$ due to the declathration process can be described by the following rate law:

$$r_{ji,\mathrm{d}} = k_{ji,\mathrm{d}} \theta_{ji}, \tag{7}$$

In other words, the corresponding molar rate $r_{ji,\mathrm{d}}$ is directly proportional to the occupancy factor $\theta_{ji}$, i.e. the fraction of cavities $i$ which are filled with guest species $j$.

As a result, we can define a local flow rate of component $j$ which results from the unbalance between adsorption and desorption:

$$F_{ji} = r_{ji,\mathrm{e}} - r_{ji,\mathrm{d}} = k_{x,\,ji,\mathrm{e}} x_{j,\mathrm{int}} (1-\theta_i) - k_{ji,\mathrm{d}} \theta_{ji} \tag{8}$$

Eq. (8) can be rewritten as:

$$F_{ji} = r_{ji,\mathrm{e}} - r_{ji,\mathrm{d}} = k_{ji,\mathrm{d}} \left( \frac{k_{x,\,ji,\mathrm{e}}}{k_{ji,\mathrm{d}}} x_{j,\mathrm{int}} (1-\theta) - \theta_j \right) \tag{9}$$

**Particular case of equilibrium**

At equilibrium, $F_{ji} = 0$ , and the following relation is derived from Eq. (9), holding for all $j \in S_{\mathrm{g}}$ , taking into account that $x_{j,\mathrm{bulk}} \equiv x_{j,\mathrm{int}} \equiv x_j$ :

$$k_{ji,\mathrm{d}} \left( \frac{k_{x,ji,\mathrm{e}}}{k_{ji,\mathrm{d}}} x_j (1-\theta) - \theta_j \right) = 0 , \tag{10}$$

With the Langmuir constants $C_{x,ji}$ defined as the ratio between the rate of enclathration and declathration according to:

$$C_{x,ji} = \frac{k_{x,ji,\mathrm{e}}}{k_{ji,\mathrm{d}}} , \tag{11}$$

Eq. (10), can be re-written as:

$$\underset{i \in S_{\mathrm{cav}}}{\forall} \; \underset{j \in S_{\mathrm{g}}}{\forall} \left( C_{x,ji} x_j (1-\theta_i) - \theta_{ji} = 0 \right) \tag{12}$$

Summing up Eq. (12) over all guest species leads to

$$\theta_i = \frac{\sum_{j' \in S_{\mathrm{g}}} C_{x,j'i} x_{j'}}{1 + \sum_{j' \in S_{\mathrm{g}}} C_{x,j'i} x_{j'}} \quad \Leftrightarrow \quad 1 - \theta_i = \frac{1}{1 + \sum_{j' \in S_{\mathrm{g}}} C_{x,j'i} x_{j'}} \tag{13}$$

Finally, by inserting Eq. (12) into Eq. (13), the following relation is derived for $\theta_{ji}$ :

$$\theta_{ji} = \frac{C_{x,ji} x_j}{1 + \sum_{j' \in S_{\mathrm{g}}} C_{x,j'i} x_{j'}} \tag{14}$$

**Enclathration during crystallization**

The surface of the crystal is supposed to be covered with cavities under formation, which can be regarded as "opened cavities" or active sites. They are assumed to cover the surface and we can define a concentration $\Gamma_i$ (number of moles of active cavities of type $i$ per unit of surface area, $[\Gamma_i] = \mathrm{mol\,m^{-2}}$). Each type of opened cavity $i$ is exposed to a rate $F_{ji}$ (mole of component $j$/mole of cavity of type $i$/unit of time). During the growth of the crystals, the rate by which the gas molecules $j$ (mole per unit of time) are incorporated into the cavities of the newly created volume is given by:

$$F_{ji} \Gamma_i A_{\mathrm{s}} \tag{15}$$

Where $A_{\mathrm{s}}$ denotes the total surface area of the growing crystals. The crystal is assumed to grow at a rate $G$ ($[G] = \mathrm{m\,s^{-1}}$). The increase in volume of the quantity of solid newly formed per element of time $dt$ is given by

$$\frac{dV}{dt} = G A_{\mathrm{s}} \tag{16}$$

The volume of the newly formed solid is composed of water molecules which build a network of cavities of different types *i*. Their molar volumetric concentration is $c_i$ (mole of cavity of type *i* per unit of volume) and they are occupied by gas molecules of type *j*. The occupancy is given by $\theta_{ji}$ (mole of component $j$/mole of cavity $i$). The flow rate by which the gas molecules *j* (mole per unit of time) are incorporated in the cavities of the new volume is:

$$c_i \theta_{ji} \frac{dV}{dt} = c_i \theta_{ji} G A_{\mathrm{s}} \tag{17}$$

Going deeply in this approach, we have showed (Herri and Kwaterski, 2012) that the approach can be simplified by defining a kinetic constant $k_j$, which is to be regarded as an intrinsic kinetic constant of component $j$

$$k_j = k_{ji,\mathrm{d}} \frac{\Gamma_i}{c_i} \tag{18}$$

Table 1 gives the new formulations of the occupancy factors depending on $k_j$ and $G$ values. The details of the calculation are given in Herri and Kwaterski (2012) and particularly how to calculate $G$ from mass transfer rates. If $G$ tends to 0, *i.e.* if the crystallization is at thermodynamic

equilibrium, it can be seen that the occupancy factors tends to the classical formulation given in eq.14. But if $G$ is non null, it can be seen that the composition of the hydrate phase during the crystallization is different from the composition that is observed at thermodynamic equilibrium.

Table 1: Occupancy factor of enclathrated molecules as a function of the composition in the liquid phase.

| | Local equilibrium resulting from a kinetic equilibrium[a] |
|---|---|
| $\theta_{ji}$ | $\dfrac{\dfrac{K_j C_{x,ji} x_{j,\mathrm{int}}}{1+k_j/G}}{1+\sum_{j'\in S_g}\dfrac{K_{j'} C_{x,j'i} x_{j',\mathrm{int}}}{1+k_{j'}/G}}$ |
| $\theta_i$ | $x_j = x_{j,\mathrm{int}}\dfrac{\dfrac{k_j}{G}}{1+\dfrac{k_j}{G}}$ $\dfrac{\sum_{j\in S_g}\dfrac{K_j C_{x,ji} x_{j,\mathrm{int}}}{1+k_j/G}}{1+\sum_{j'\in S_g}\dfrac{K_{j'} C_{x,j'i} x_{j',\mathrm{int}}}{1+k_{j'}/G}}$ |
| $1-\theta_i$ | $\dfrac{1}{1+\sum_{j\in S_g}\dfrac{K_j C_{x,ji} x_{j,\mathrm{int}}}{1+k_j/G}}$ |

[a] The Langmuir coefficient is usually calculated by using a modified Kihara approach in which the mole fraction $x_j$ of the guest component $j$ is replaced by the corresponding fugacity $f_j$. Expressing the relation between the Langmuir coefficients $C_{x,ji}$ and $C_{f,ji} = C_{ji}$ as $C_{x,ji} x_j = C_{ji} f_i$, an approximate relation can be derived for calculating $C_{x,ji}$ as a function of $C_{ji}$ by using a simplified version of Henry's law in the form of $f_j = x_j k^{\infty}_{H,j\mathrm{w}} \exp(pV^{\infty}_{\mathrm{m},j}/RT)$, where liquid phase non-idealities expressed by means of the activity coefficient as well as the pressure dependence of $V^{\infty}_{\mathrm{m},j}$, the partial molar volume of $j$ at infinite dilution, are neglected. In this relationship $k^{\infty}_{H,j\mathrm{w}}$ is Henry's constant of the guest species $j$ in the solvent water at the saturation pressure of the solvent. By proceeding in that way, the approximate relation $C_{x,ji} = C_{ji} k^{\infty}_{H,j\mathrm{w}} \exp(pV^{\infty}_{\mathrm{m},j}/RT)$ is obtained.

## DETERMINATION OF THE LANGMUIR CONSTANTS

The expression of the occupancy factor $\theta_{ji}$ at equilibrium is given by eq.14 and expressed here in term of fugacity:

$$\theta^i_j = \frac{C_{f,ji} f_j(T,P)}{1+\sum_j C_{f,ji} f_j(T,P)} \tag{19}$$

Where $C_{f,ji}$ is the Langmuir constant of component j in the cavity i. It describes the interaction potential between the encaged guest molecule and the surrounding water molecules evaluated by assuming a spherically symmetrical cage that can be described by a spherical interaction potential:

$$C^i_j = \frac{4\pi}{kT}\int_0^{\infty} \exp\left(-\frac{w(r)}{kT}\right) r^2 dr \tag{20}$$

Where $w(r)$ is the interaction potential between the cavity and the gas molecule according to the distance $r$ between the guest molecule and the water molecules over the structure. The interaction potential can be determined by different models such as e.g. the van der Waals and Platteeuw model (1959), the Parrish and Prausnitz model (1972) or the so-called Kihara model. The latter, being the most precise (MacKoy and Sinagoglu, 1963), $w(r)$ can be expressed as:

$$w(r) = 2z\varepsilon\left[\frac{\sigma^{12}}{R^{11} r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^6}{R^5 r}\left(\delta^4 + \frac{a}{R}\delta^5\right)\right] \tag{21}$$

$$\delta^N = \frac{1}{N}\left[\left(1-\frac{r}{R}-\frac{a}{R}\right)^{-N} - \left(1+\frac{r}{R}-\frac{a}{R}\right)^{-N}\right] \tag{22}$$

The gas parameters $\varepsilon$, $\sigma$ and $a$ are the so-called Kihara parameters and can be calculated from experimental data by fitting the model equations to corresponding hydrate equilibrium experimental data, following a procedure given in Herri et al. (2011).

In this description, the interaction potential becomes only dependent on the properties of gases (*via* the Kihara parameters), and dependent of geometrical properties of the cavities (*via* their coordination number *z* and radius *R*)

## DETERMINATION OF KIHARA PARAMETERS

As we mentioned, the crystallization of gas mixture hydrates gives necessary non equilibrium gas hydrates (Table 1), once the growing rate is non null. The only way to obtain gas mixture hydrates at equilibrium is to operate the crystallization at a very low rate, *i.e.* with a very low driving force. So, the determination of Kihara parameters can be done only from pure gas equilibrium data for which there is no doubt on the composition the hydrate phase.

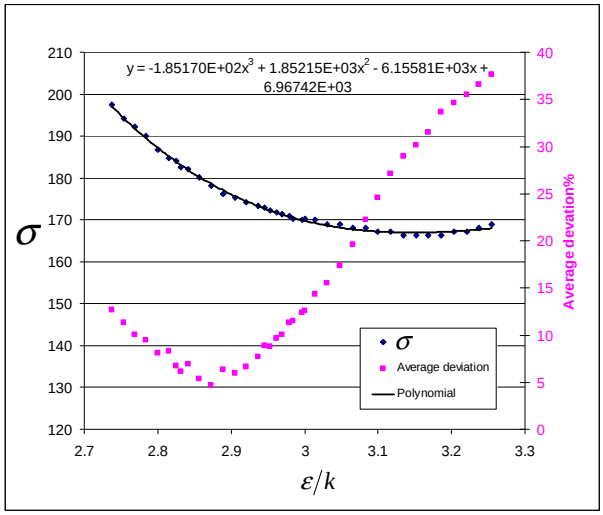


Figure 3.ε/k versus σ at the minimum deviation with experimental data (range of temperature from 151.52K to 282.9K and a pressure range from 0.535kPa to 4370kPa, from Herri and Chassefière, 2012).

### Carbon dioxyde Kihara parameters

In the work of Herri and Chassefière (2012), the Kihara parameters have been retrieved for pure $CO_2$ clathrate hydrate by assuming a SI structure.
It is an optimal situation because the equilibrium data are numerous. The study compares 32 experimental results which cover a range of temperature from 151.52K to 282.9K and a pressure range from 0.535kPa to 4370kPa.

On **Erreur ! Source du renvoi introuvable.**, we can see the $\varepsilon/k$ and $\sigma$ values which can verify the equilibrium conditions given in Eq.(1), and the corresponding mean deviation $F$ between the experimental data and the model, given by :

$$F(\varepsilon_j, \sigma_j) = \sum_{l=1}^{N} \left| \frac{P_{calc}}{P_{\exp}} - 1 \right| \tag{23}$$

We can see that the deviation presents a clear minimum which can be considered as the best values of $\varepsilon/k$ and $\sigma$ (reported in Table 2).

### Methane Kihara parameters

The Kihara parameters have been retrieved for pure $CH_4$ clathrate hydrate by Herri and Chassefière (2012) by assuming a SI structure. The equilibrium data are also numerous. The study compares from a set of 27 experimental results which cover a range of temperature from 145.75 to 286.4K and a pressure range from 2.4kPa to 10570kPa. On Figure 4, the deviation presents a clear minimum which can be considered as the best values of $\varepsilon/k$ and $\sigma$ (reported in Table 2).

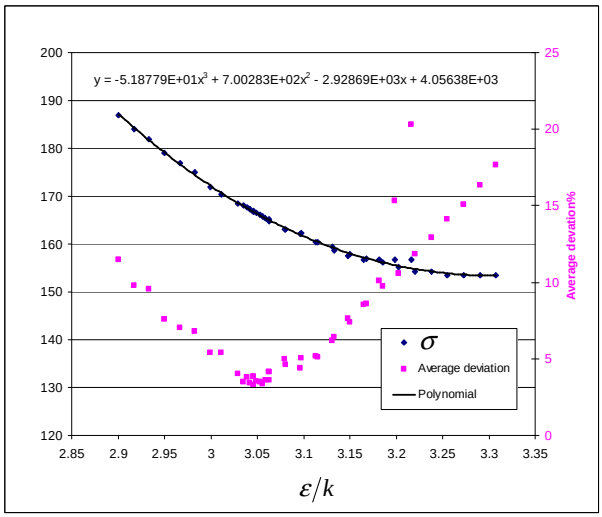


Figure 4. ε/k versus σ at the minimum deviation with experimental data (range of temperature from 145.75 to 286.4K and a pressure range from 2.4kPa to 10570kPa, from Herri and Chassefière, 2012)

### Ethane Kihara parameters

In this work, the Kihara parameters have been retrieved for pure ethane clathrate hydrate by assuming a SI structure. The equilibrium data are

numerous and 61 experimental results have been retained for the optimisation, from Robert et al. (1940), Deaton and Frost (1946), Reamer et al. (1952), Falabella (1975), Yasuda and Ohmura (2008), Mohammadi and Richon (2010), which cover a wide range of temperature from 200.08 to 287.4K and a pressure range from 8.3kPa to 3298kPa. On Figure 5, the deviation presents a clear minimum which can be considered as the best values of $\varepsilon/k$ and $\sigma$ (reported Table 2).

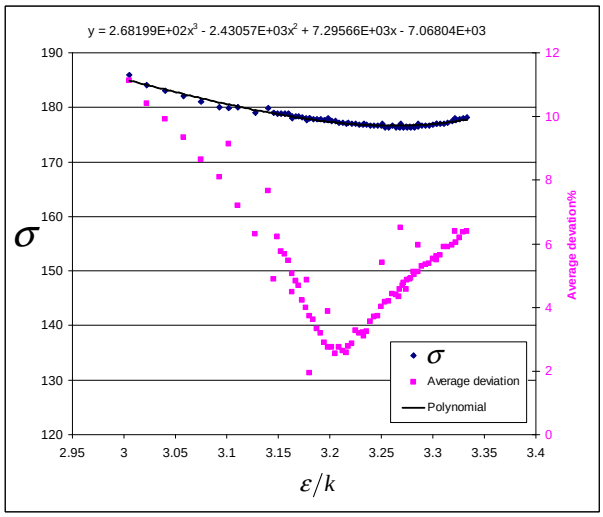


Figure 5. ε/k versus σ at the minimum deviation with experimental data (range of temperature from 200.08 to 287.4K and a pressure range from 8.3kPa to 3298kPa).

**Propane Kihara parameters**

The Kihara parameters have been retrieved for pure propane clathrate hydrate by assuming a SII structure. The equilibrium data are numerous but does not cover a wide temperature range. 41 experimental results have been retained for the optimisation of the kihara parameters from Yasuda and Ohmura (2008), Deaton and Frost (1946) and Nixdorf and Oellrich (1997) which cover a range of temperature from 245 to 278.5K and a pressure range from 41kPa to 567kPa.

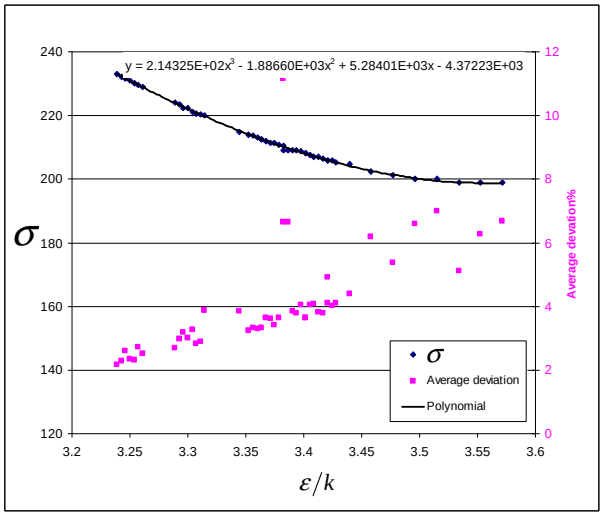


Figure 6. ε/k versus σ$\sigma$ at the minimum deviation with experimental data (from Yasuda and Ohmura 2008, Deaton and Frost 1946 and Nixdorf and Oellrich 1997,which cover a wide range of temperature from 245 to 278.5K and a pressure range from 41kPa to 567kPa).

On **Figure 6**, the deviation does not present a minimum. So, the kihara parameters can not be retrieved directly from the pure gas equilibrium data. The experimental data bank needs to be extended to other equilibrium data, and especially to two components gas mixtures, with a second gas which kihara parameters are well known. Also, we need to be sure that the data are really at equilibrium before fitting the kihara parameters.So, in this work, the kihara parameters from propane gas are not retrieved.

| | $\frac{\varepsilon}{k}$ | $a$ | $\sigma$ |
|---|---|---|---|
| $CO_2$ | 178.21(\$) | 0.6805(+) | 2.873(\$) |
| $CH_4$ | 166.36(\$) | 0.3834(+) | 3.050(\$) |
| $C_2H_6$ | 177.46(*) | 0.5651(+) | 3.205(*) |

(*)-regressed from this work, (+)-from Sloan (1998,2005), ($)-from Herri and Chassefière (2012)

Table 2 Kihara parameters, after optimisation from experimental data with the GasHyDyn simulator, implemented with $\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta,0}$ *and* $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta,0}$ values from Handa and Tse (1986). and $\Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\Big|_T$ , $\Delta c_{p,\mathrm{w}}^{\mathrm{L}-\beta,0}$ and $b_{p,\mathrm{w}}^{\mathrm{L}-\beta}$ from Sloan (1998).

## EQUILIBRIUM DATA FROM CO2-C1-C2 GAS MIXTURES

We performed experimental data on the CO2-C1-C2 gas mixture, by using two different operative protocols, one which can be considered at high rate of crystallization, and the other one which can be considered at low rate of crystallization (Bouillot et al, 22014, ICGH8).
The first operative protocol consists in cooling down the liquid solution to the operative temperature at atmospheric pressure, to reach an operative condition outside the formation zone. Then, the pressure is suddenly increased to enter deeply in the formation zone.
The second method consists in increasing first the pressure, at a high temperature to reach a starting point located outside the hydrate formation zone. Then, the temperature is decreased by steps of 0.1°C per day to initiate low rate crystallization.

The data and experimental procedure are given in Bouillot et al (ICGH8, 2014). If we consider the model as the reference, we can say that the experimental data converge to the model as the rate of crystallization is lowered (see table 3). So, if the rate of crystallization is lowered, the hydrate formation tends to be performed at equilibrium, and the hydrate composition can be modeled from the thermodynamic model. If the crystallization is operated at high rate, the hydrate composition is different from the model, and we can consider that the hydrate are formed under non equilibrium conditions. In that case, we need to focus on a new way to model the hydrate composition, and it is the reason that we proposed a new model to couple the thermodynamics and the kinetics (Herri and Kwaterski, 2012, see Table 1)

| Mean deviation (exp. results versus GasHyDyn) | | | | |
|---|---|---|---|---|
| Gas | P | Molar fraction (in hydrate) | | |
| | | $CO_2$ | $CH_4$ | $C_2H_6$ |
| 8* | 8.7% | 35.0% | 6.0% | 144.0% |
| 12* | 1.8% | 24.1% | 5.3% | 11.6% |

Table 3 Standard deviation (%) between experimental results from Bouillot et al. (2014)* and GasHyDyn (thermodynamic modelling work).

## VALIDATION OF THE MODEL AGAINST OTHER DATA

### *$CO_2$ - $CH_4$ binary gas H-Lw-V equilibria:*

The literature is well documented, and proposes equilibrium data giving Pressure, Temperature, Gas Composition, and sometimes Hydrate Composition.

The data from the Ph.D. work of Bouchemoua (Herri et al, 2011), are an important validation for us, because they are from our laboratory with the same experimental procedure. The model predicts both the equilibrium pressure (with a precision of 2.14%) but also the composition of gas in the hydrate phase, with a very good precision of 2 % for $CO_2$, and a better precision of 1.4% for $CH_4$. Unfortunately, the data are few, 6 equilibrium points at the temperature of 4°C, in the range of pressure of [2.04-3.9 MPa] and range of molar fraction of [0-1].

The validity of the model is maintained, with less precision, if applied to our experimental results from this work (ICGH8, Bouillot et al, 2014). We measured 14 equilibrium points, in the range of temperature of [2.2-9.5°C], range of pressure of [2.91-5.6 MPa] and range of $CO_2$ molar fraction of [0.147-0.77]. The model predicts both the equilibrium pressure (with a precision of 3.8%) but also the composition of gas in the hydrate

phase, with a correct precision of 15.7 % for $CO_2$, and a correct precision of 11.7% for $CH_4$

The comparison to the experimental results from Belandria et al (2011) is also a fruitful comparison, because it is an external source, but using an experimental protocol inherited from us. During their work, in collaboration with us in the framework of a national projet (ANR SECOHYA), they measured 40 equilibrium points in the range of temperature of [0.45-11.05°C], range of pressure of [1.51-7.19 MPa] and range of $CO_2$ molar fraction of [0.081-0.669]. The model predicts both the equilibrium pressure (with a precision of 7.8%) but also the composition of gas in the hydrate phase, with an acceptable precision of 18.8 % for $CO_2$, and a correct precision of 21.4% for $CH_4$.

Ohgaki et al (1996) has given 31 equilibrium data , at temperature of 7.15°C, range of pressure of [3.04-5.46 MPa] and range of $CO_2$ molar fraction of [0-1] . The accuracy of the model in this case is comparable to the prediction accuracy with our experimental data. The equilibrium pressure is predicted with a precision of 5.9%), the composition of gas in the hydrate phase is simulated with a good precision, 15.4 % for $CO_2$, and 14.4% for $CH_4$.

The experimental data from Seo et al (2000) can be regarded as a very good case study. They gave 14 equilibrium data in the range of temperature of [-0.05-7.35°C], range of pressure of [2-3.5 MPa] and range of $CO_2$ molar fraction of [0.133-0.834]). The pressure is predicted with a very good precision of 3.3%, but the simulation of composition of the hydrate phase is totally un-correct, 34.8 % for $CO_2$, and 866.5% for $CH_4$. In fact, their hydrate phase seems to be considerably $CO_2$ enriched and it can be explained only from kinetic considerations. For us, it gives evidence that, for gas mixtures, the simulation of the correct equilibrium pressure is not enough to validate the exactness of the kihara parameters. Also, we can say that the experimental results of Seo et al (2000) are clearly different to the others experimental results from our work and previous works from Bouchemoua et al (2011), Belandria et al (2011) and Oghaki et al (1996).

Other experimental data are available in the literature, but they don't give the hydrate composition at the equilibrium, only the Temperature, Pressure and Gas Composition. Given the temperature, the model predicts the equilibrium pressure:

- Adisasmito et al (1999), precision of 4.5% ,
- Hachikuko et (2002), precision of 4.6 %,
- Unruh and Katz (1929), precision of 8.2 % .

### *$CO_2$ - $C_2H_6$ binary gas H-Lw-V equilibria:*

Only one open source can be found in the literature, from Adisasmito and Sloan (1996) It gives 14 equilibrium data, at temperature of [0.55-14.65°C], range of pressure of [0.57-3.83 MPa] and range of $CO_2$ molar fraction of [0.189-0.417]. The composition of the hydrate phase is not given. The prediction of the model to their equilibrium data is 19.9%, a not correct value in our understanding.

### *$CH_4$ - $C_2H_6$ binary gas H-Lw-V equilibria:*

There is no source giving the hydrate composition versus equilibrium, only Temperature, Pressure and Gas Composition.

Deaton and Frost (1946) have given 22 equilibrium data, at temperature range of [1.65-10.05], range of pressure of [1.289-6.088 MPa] and range of $CH_4$ molar fraction of [0.564-0.988]. . The prediction of the model to pressure is 11.0%. The composition of the hydrate phase is not given.

Holder and Grigouriou (1980) have given 22 equilibrium data, at temperature range of [6.25-14.65], range of pressure of [0.99-3.08 MPa] and range of $CH_4$ molar fraction at very low value of [0.016-0.047]. The prediction of the model to pressure is 6.3%. Due to the very low concentration of methane, the validation of the model via the simulation of the equilibrium pressure concerns more the validation of the kihara parameters of ethane rather than methane. But, because the composition of the hydrate phase is not given, this validation is partial.

## CONCLUSIONS

We consider that the Kihara parameters of $CO_2$, $CH_4$ and $C_2H_6$ have been correctly estimated from pure gas equilibrium curves. The literature data are rich enough to cover a wide range of temperature and a wide range of pressure, and the optimisation of the kihara parameters clearly give a single solution.

If applied to gas mixture, we can say that:

In some cases, the model predicts very well the equilibrium data, especially for the $CO_2$-$CH_4$ gas mixture, that is very well documented. This observation is very important because it allows to validating our experimental procedure. In fact, we get now an amount of experimental data on our side, from this work, or from previous works (Bouchemoua et al, 2011), or from literature (Belandria et al, 2011, and Oghaki et al, 1996), that can be simulated with the same model.

In other cases of $CO_2$-$CH_4$ gas mixture, we can observe one set of data (Seo et al, 2000) for which we can model the equilibrium pressure, but not the hydrate composition, whereas for all the other experimental data sources, the composition was pretty well modeled.

For $CO_2$-$C_2H_6$ and $CH_4$-$C_2H_6$ gas mixtures, we do not have data to validate the model against the hydrate composition. However, the modeling of the equilibrium pressure (given temperature and gas composition) is correct for $CH_4$-$C_2H_6$ (precision less than 11%) but could be not acceptable for $CO_2$-$C_2H_6$ (precision around 20%)

For the ternary system $CO_2$-$CH_4$-$C_2H_6$ investigated, we can do a clear difference in between the experimental data with a crystallization at high rate, where the model does not fit the data, and the experiments at low crystallization rate where there is a convergence toward the model.

In our understanding, these experimental facts confirm our original intuition that the hydrate could not form under equilibrium once the gas is a mixture (for example the ternary system $CO_2$-$CH_4$-$C_2H_6$),. If the crystallization is operated very slowly close to the thermodynamic equilibrium conditions, the hydrate composition tends to be at equilibrium. Nevertheless, they can also form at thermodynamic equilibrium (for example in the major part of the $CO_2$-$CH_4$ experimental data) even if the crystallization is operated at high rate.
So, it is a source of confusion, especially if a component is not documented enough, to the optimization of the Kihara parameters from the single gas hydrate equilibrium curve. In that case, we need to extend the data base to gas mixtures with the risk that hydrates are not formed under equilibrium in these cases, and so, that the data used for the parameters regression are not representative of the thermodynamic equilibrium.

For us, these new considerations open a new field of modeling: trying to simulate the composition of the gas hydrate during non equilibrium conditions, In fact, it is clear for us that the hydrate composition is not systematically given from classical thermodynamic modeling, but needs to take into account kinetic steps also, such as the mass transfer barriers, or the growth rate, which affect deeply the hydrate composition as we recall in Table 1.

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