Gas hydrate equilibria for CO2–N2 and CO2–CH4 gas mixtures-Experimental studies and thermodynamic modelling

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Gas Hydrate Equilibria for CO_2-N_2 and CO_2-CH_4 gas mixtures – Experimental studies and Thermodynamic Modelling

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Abstract

In this paper, a set of experimental data on the phase equilibrium of gas hydrates in the presence of binary gas mixtures comprising CO_2 is presented. The procedure established allows for the determination of both the composition of the gas phase as well as the hydrate phase without the need to sample the hydrate. The experimental results obtained in these measurements have been described by means of the classical model of van der Waals and Platteeuw. The values of internal parameters of the reference state and the Kihara parameters have been re-discussed and their interdependency is pointed. Finally the new set of parameters is validated against experimental data from other sources available in the literature, or invalidated against other sources. Finally, we conclude on the difference of experimental data between laboratories. The differences are not on the classical (Pressure, Temperature, gas composition) data which appear equivalent between laboratories. The difference stands on the measurement composition of the hydrate phase.

Keywords: gas hydrates, thermodynamic, crystallization, modeling

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1

1 Introduction

CO_2 capture in industry is a challenge that is suitable for reducing the global carbon emissions. The gases emitted by industry are by definition localized at the plants, like e.g. steelmaking plants, gas or coal power plants, chemical plants or natural gas production plants. For that reason it is envisaged to employ industrial process to remove those industrial gases that have an impact on the global warming before being emitted into the atmosphere. However, in designing processes for removal of these green house gases, it is very important to consider the quantities to be treated. In case of steelmaking plants for example, the emissions can be in the order of several cubic meters per second of CO_2. In power plants, the concentration of CO_2 is generally low, typically in the range of 5-15%, but it can be several tens of percents in steelmaking plants or in some cases of natural gas production.

Facing the variety of gases to be treated with regard to their quantities, qualities (mainly the CO_2 content, but also the presence of minor impurities such as H_2S, SO_2, NO_X....), and conditions of pressure and temperature, different strategies and technologies need to be developed to minimize the cost of the process.

Hydrate technology could be an alternative approach to remove green house gases and this is the route we try to develop. A preliminary costing has revealed the process to be competitive for high concentrated mixtures of CO_2 containing N_2 (Nuyeng et al, 2007) such as found in exhaust gases of steel making plants at atmospheric pressure.

Currently we are working on the accurate modeling of hydrate equilibria in the presence of multiple gas components. The respective routines are to be implemented into process simulation software allowing for the precise evaluation of different sizing and costing schemes of capture. This work presents a set of experimental data on the CO_2-N_2 and CO_2-CH_4 hydrate equilibria with pure water. We present in detail our experimental procedure by

which the gas composition can be measured directly, whereas the hydrate composition is to be calculated from a mass balance.

Furthermore we have tried to validate our experimental data by using the classical van der Waals and Platteeuw model (1959) with internal parameters found in the literature. These parameters are the so-called macroscopic parameters (i.e. macroscopic parameters from Table 3 which refer to a classical thermodynamic approach) and the so-called Kihara parameters (referring to a statistical approach).

Due to large deviations between the modeled values obtained in the way described above and the experimental results, we have re-fitted the internal parameters, essentially by retaining a set of macroscopic parameters from Handa and Tse (1986), and re-fitting the Kihara parameters from our experimental results. Finally the new set of parameters is validated against experimental data from other sources available in the literature, or invalidated against other sources.

2   Gas Hydrates
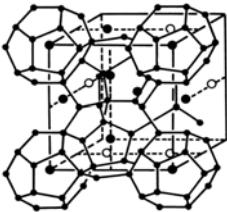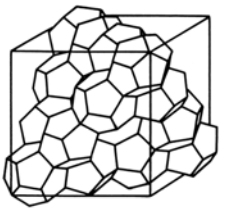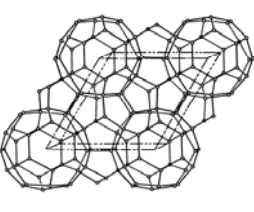
The clathrates are ice-like compounds in the sense that they correspond to a re-organisation of the water molecules to form a solid. The crystallographic structure is based on H-bonds. The clathrates of water are also designated improperly as "porous ice" because the water molecules build a solid network of cavities in which gases, volatile liquids or other small molecules could be captured.

The clathrates of gases, called gas hydrates, have been studied intensively due to their occurrence in deep sea pipelines where they cause serious problems of flow assurance.

Each structure is a combination of different types of polyhedra sharing faces between them. Jeffrey (1984) suggested the nomenclature e^f to describe each polyhedra: e is the number of edges of the face, and f is the number of faces with e edges. Currently, three different

structures have been established precisely, called I, II and H (Sloan, 1998, Sloan and Koh, 2007)

Table 1   Structure of gas hydrates

	SI		SII		SH		
Cavity	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$	5^{12}	$4^35^66^3$	$5^{12}6^8$
Type of cavity (j: indexing number)	1	2	1	3	1	5	4
Number of cavities (m_j)	2	6	16	8	3	2	1
Average cavity radius (nm)(1)	0.395	0.433	0.391	0.473	0.391	0.406	0.571
Variation in radius, % (2)	3.4	14.4	5.5	1.73			
Coordination number	20	24	20	28	20	20	36
Number of water molecules	42		136		134		
Cell parameters (nm)	a= 1.1956 (3)		a=1.7315 (4)		a=1.2217, b=1.0053 (5)		
Cell volume (nm^3)	1.709 (3)		5.192 (4)		1.22994 (5)		

(1) Sloan (1998, p. 33).
(2) Variation in distance of oxygen atoms from centre of cages (Sloan, 1998, p. 33).
(3) For ethane hydrate, from (Udachin, 2002).
(4) For tetrahydrofuran hydrate, from Udachin (2002).
(5) For methylcyclohexane-methane hydrate, from Udachin (2002).

3   Experimetal procedure and set-up

3.1   Experimental set-up

An experimental apparatus (Fig. 1) has been built to investigate the thermodynamic equilibrium conditions of gas hydrates (pressure and temperature) and to determine the composition of all existing phases (gas, liquid and hydrate). The experimental set-up consists of a stainless steel high pressure batch reactor (Autoclave) with a double jacket connected to an external cooler (HUBERT CC-505) with a CC3 controller maintaining the temperature with a precision of 0.02 K. Two sapphire windows of (12 x 2 cm) mounted on both sides of the reactor enable to detect the occurrence of a hydrate phase by direct visual observation. A Pyrex cell is located in the stainless steel autoclave in which the pressure can be raised up to

10 MPa. The Pyrex cylinder is filled with 800 ml to 1 l of water containing $LiNO_3$ as an anionic tracer at a concentration of approximately 10 to 15 ppm (weight). The liquid is injected in the pressurized reactor by using a HPLC pump (JASCO-PU-1587). A four vertical-blade turbine impeller ensures stirring of the suspension during crystallization. The temperature is monitored by two Pt100 probes, one in the liquid bulk, and the other one in the gas phase (Prosensor instrument, precision of 0.02 K). The pressure is measured by mean of a pressure transducer (range: 0–10 MPa (Keller instrument, precision of 0.05 MPa). The data acquisition unit (T, P) is connected to a personal computer. The composition of the gas phase is determined in line by using a gas chromatograph after sampling by a ROLSI instrument. This tool collects a controlled volume of gas (some μm^3) which is directly injected into the loop of the gas chromatograph (VARIAN model CP-3800 GC). The precision in gas composition is 2% (see annex 1)

A classical valve is used to take a sample of 1 ml of liquid which is directed to a DIONEX ionic exchange chromatograph (off-line) to measure the tracer ($LiNO_3$) concentration. The tracer is an ionic element which is not incorporated into the hydrate structure but concentrated in the liquid phase during crystallization.

The gas mixtures are prepared by injecting each gas directly into the reactor. The mixtures are analyzed by gas chromatography to obtain the exact composition of each gas (see annex 1)

1. Cryostat
2. Reactor sell 2L, 100 bars
3. Sapphire Windows 12x2 cm
4. Gas cylinder
5. Stirrer
6. Temperature sensor (Pt 100)
7. Liquid sampling
8. HPLC pump
9. FBRM probe (LASENTECH)
10. ROLSI gas sampling
11. In line gas Chromatograph
12. Helium alimentation
13. Pressure and temperature view
14. Data acquisition
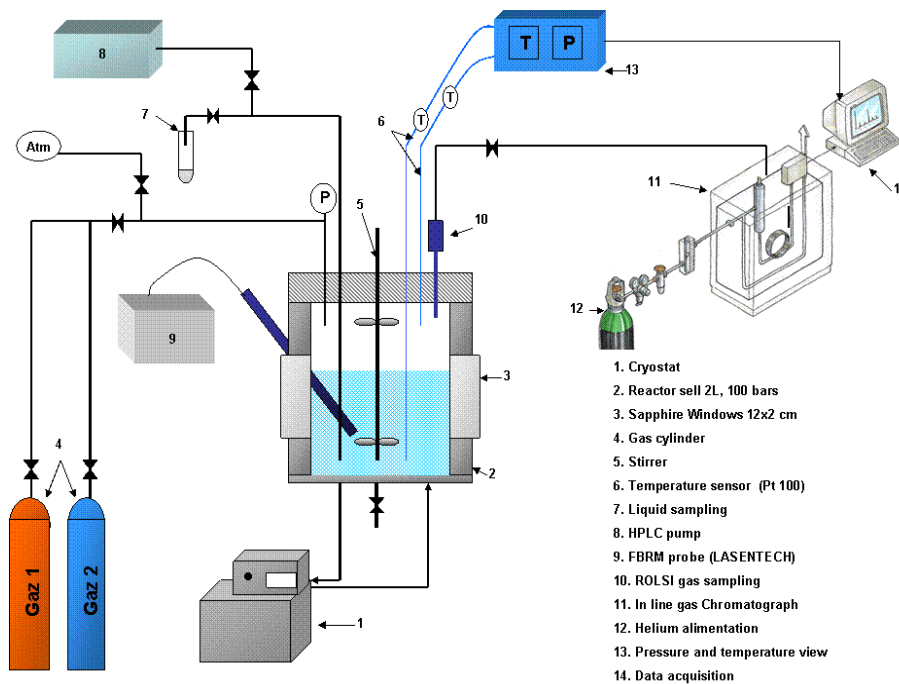
Fig. 1   Experimental setup

3.2   Experimental procedure

The hydrate is obtained by crystallization of gas mixtures (CO_2 with N_2 or CH_4) in presence of a liquid phase (water + $LiNO_3$ (10 ppm weight fraction)).

Initially the reactor is closed and evacuated by means of a vacuum pump. Subsequently, the cell is flushed three times with nitrogen (or CH_4, depending on the experiment) to eliminate any trace of other gases (e.g. from a preceding experimental run). After this cleaning procedure, the reactor is evacuated again.

At the beginning of the actual experimental run, the reactor is pressurized with the first gas (generally this has been CO_2 because the maximum pressure in the CO_2 bottle is about 5 MPa). Subsequently the second gas (N_2 or CH_4) is injected until the operative pressure is reached (up to 10 MPa depending on the experiments). The gas mixture is stirred and cooled down, and then maintained at the operative temperature (typically in the range from 0 to 10 °C)

The stirrer is then stopped and the liquid solution (1 l) is injected in the reactor by using the HPLC pump. Upon injection of the solution an increase of both temperature as well as pressure is observed simultaneously, firstly because the liquid is at ambient temperature, and also as a consequence of the gas compression resulting from the reduction of the gas volume by the liquid injection.

The stirrer is started. A decrease of the pressure is detected due to partial dissolution of the gaseous components in the liquid phase. After a while (ranging from some minutes to several hours, since nucleation being a stochastic phenomenon), crystallization (exothermic process) starts accompanied by a sudden increase of temperature that depends on the intensity of the crystallization (33 h on Fig. 2). During the formation of the solid, the pressure decreases due to the gas consumption to form hydrates. During the crystallization, the gas phase is sampled with the ROLSI© instrument and analyzed by in-line gas chromatography. The liquid phase is sampled to be analyzed off-line by ion exchange chromatography. After a while, the system reaches equilibrium (end of crystallization), and correspondingly the values of pressure and temperature approach constant values.

The gas hydrate dissociation is operated at constant volume and started by heating the reactor in increments of 1°C (Fig 3). After each increment of temperature, the pressure increases due to gas hydrate dissociation and reaches a constant value which represents the thermodynamic equilibrium. In the same way as in the case of the crystallization steps, the gas and the liquid phases are sampled to determine the compositions of the phases at equilibrium (the calculation method is presented in the next section).
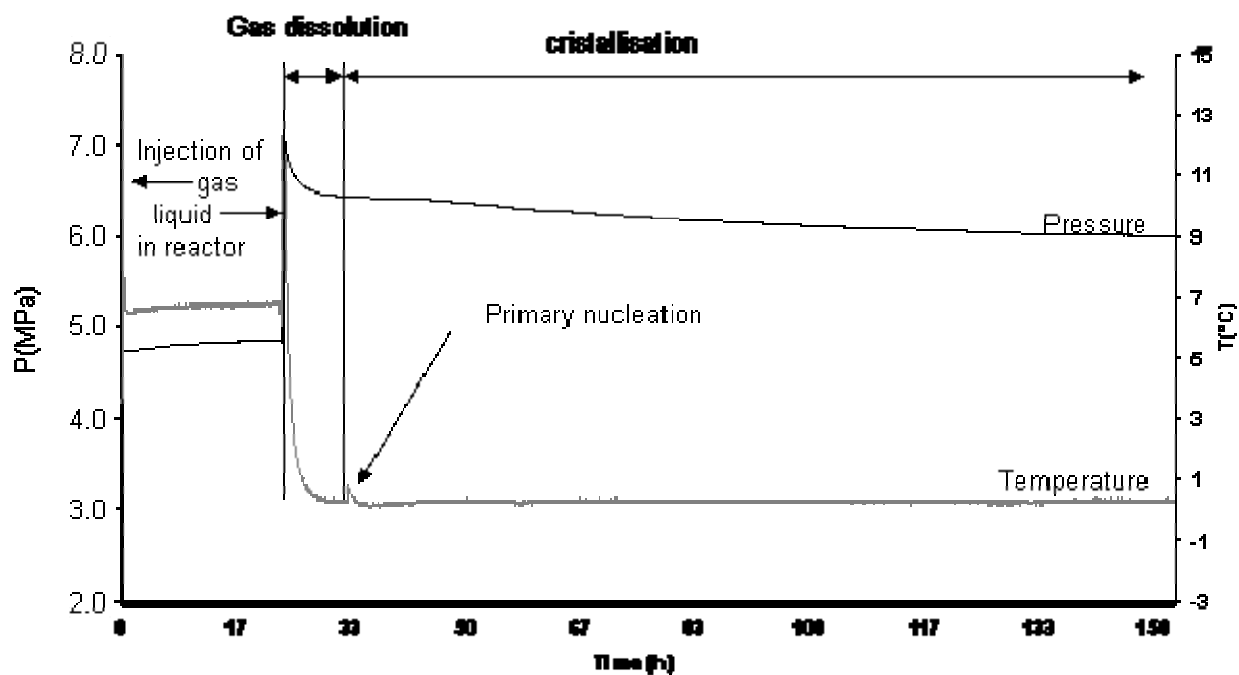
Fig. 2   Evolution of pressure and temperature during crystallization
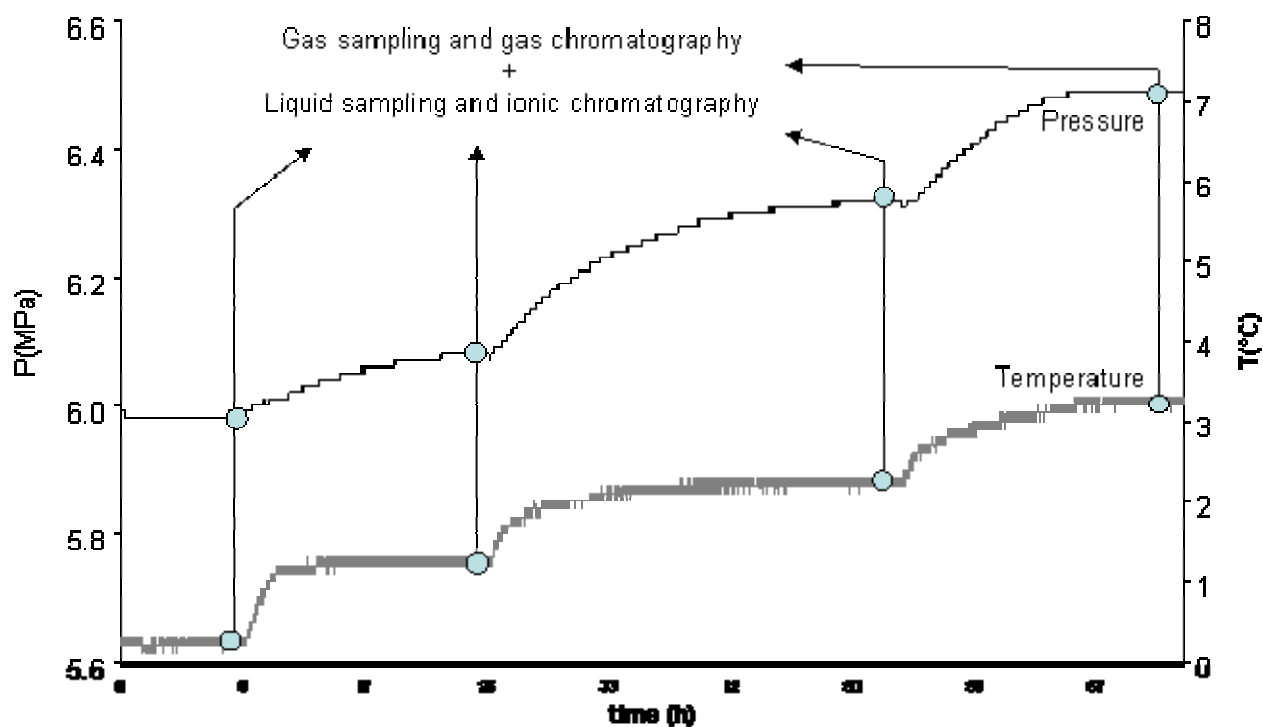
Fig. 3   Evolution of pressure and temperature during dissociation

3.3 Gas composition in the different phases

In order to calculate the mole number of each gas in the different coexisting phases, a mass balance is set up for each of the gaseous components j ($j = CO_2, CH_4, N_2$).

3.3.1 The mass balance for the gaseous components

When at given values of the state variables, a gaseous, a liquid and a solid hydrate phase are present in the system the initial quantity of the gases in the reactor is distributed between these three phases. Thus, in equilibrium, the quantity of gas in the hydrate phase can be determined from a mass balance according to:

$$n_{j,0} = n_j^H + n_j^L + n_j^G \qquad (1)$$

In eq. (1), $n_{j,0}$ stands for the initial (total) mole number and n_j^H, n_j^L and n_j^G are the mole numbers of the gaseous component j ($j = CO_2, CH_4, N_2$) in the hydrate, the liquid and the gas phase, respectively.

The amount of substance of the gases dissolved in the liquid phase is then estimated by means of corresponding gas solubility data, whereas the mole number of the gases present in the gas phase is calculated by using an equation of state approach as outlined in the next sections.

3.3.2 Composition and amounts of substance of the gases in the gas phase

The total mole number n^G in the gas phase in any equilibrium state can be calculated by means of the classical Eq. (2)

$$Z(T, p, \vec{y}) = \frac{PV}{nRT} \qquad (2)$$

for $n \equiv n^G$. In Eq. (2), T, P, and V are the temperature, pressure and total volume, respectively, while $\vec{y} = (y_1, \ldots, y_N)$, n and R represent the vector of the mole fractions of the components in the mixture, the total mole number in the gas mixture, and the universal gas constant, respectively. Z is the compressibility factor that can be calculated by means of a suitable equation of state (EOS), e.g., a classical cubic EOS. For the data evaluation in this study, the Soave-Redlich and Kwong (SRK) EOS has been used (parameters from Danesh, 1998).

Before, during the crystallization, or at equilibrium, the composition of gas in the gas phase is determined by using gas chromatographic analysis.

We recall here that the reactor of total inner volume $V_R = 2.52$ l is initially filled with the gaseous components at the initial temperature T_0 and under the initial total pressure P_0. Therefore, at this stage, the system consists of a gas phase only, being composed of the two gaseous components j and k, each of which having the initial mole fractions $y_{j,0} = 1 - y_{k,0}$ ($j, k = CO_2, CH_4, N_2; j \neq k$). Utilising the results from the measurements of temperature, pressure, and the gas chromatographic analysis, the initial total mole number in the gas phase n_0^G is derived from Eq. (2) according to

$$n_0^G = \frac{P_0 V_R}{Z(T, p, y_{j,0}) R T_0}, \tag{3}$$

where the composition of the gas phase has been determined analytically by means of the gas chromatographic analysis.

Eq. (2) has also been used to determine the total amount of substance of the gas phase in a state corresponding to the three phase hydrate-liquid-vapour equilibrium. In the latter case, the initial values of the variables are to be replaced by the corresponding values measured in that equilibrium state, i.e., T_0, P_0, $y_{j,0}$ and n_0^G are to be substituted for T, P, y_j and n^G. The

volume of the reactor V_R has been replaced by the actual value of the gas phase V^G, which for

any given equilibrium state has been approximated by:

$$V^G = V_R - V_{w,0} \qquad (4)$$

where $V_{w,0}$ stands for the volume of the liquid water, the reactor is initially loaded with.

With the total mole numbers in the gas phase n_0^G and n^G derived in the way described above,

the mole numbers of the respective gaseous component j ($j = CO_2, CH_4, N_2$) in the gas

phase, $n_{j,0}^G$ and n_j^G, are respectively given by:

$$n_{j,0}^G = n_0^G y_{j,0} \quad \text{and} \quad n_j^G = n^G y_j \qquad (5)$$

3.3.3   The liquid phase volume

As mentioned before, the liquid phase contains LiNO₃ as a tracer. Initially the concentration

of lithium $[Li^+]_0$ and the initial volume of liquid V_0^L are known. During the crystallization

and dissociation steps, the concentration of lithium is measured by ion-exchange

chromatography after sampling. So, we can calculate the volume of liquid water from a mass

balance for the Li^+ ions:

$$V_0^L [Li^+]_0 = V^L [Li^+] \quad \Rightarrow \quad V^L = \frac{V_0^L [Li^+]_0}{[Li^+]} \qquad (6)$$

where V^L and $[Li^+]$ are the volume of the liquid aqueous phase and the molar concentration

of lithium in this phase, i.e., in the sample, corresponding to a given step of the crystallization

or dissociation.

3.3.4   Composition of the liquid phase

The mole number of gas in the liquid phase Eq. (13) is calculated in a good approximation by

using solubility data of the gas in water (Holder , 1980) under the assumption that LiNO₃, due

11

to its low concentration (10 ppm), does not affect this solubility. In equilibrium, the equality of the fugacities of the gases in the liquid and the gas phase holds according to

$$f_j^{\mathrm{L}}(T,P,x_j) = f_j^{\mathrm{G}}(T,P,y_j),$$ (7)

Substitution of the fugacity in the liquid phase for an extended form of Henry's law and expressing the fugacity in the gas phase in terms of the gas phase fugacity coefficient in Eq. (9), leads to an expression for the mole number n_j^{L} of the gas j dissolved in the liquid phase:

$$n_j^{\mathrm{L}} = \frac{V^{\mathrm{L}} \rho_{\mathrm{w}}^{\circ}}{M_{\mathrm{w}}} \frac{y_j \varphi_j^{\mathrm{G}} P}{K_{\mathrm{H},j}^{\infty} \exp\left(P v_j^{\infty}/RT\right)}$$ (8)

In Eq. (8), $V^{\mathrm{L}} \cong V_{\mathrm{w}}^{\mathrm{L}}$ stands for the volume of the liquid phase in equilibrium, $\rho_{\mathrm{w}}^{\circ}$ is the density, and M_{w} is the molar mass of pure water. $v_j^{\infty} = 32~\mathrm{cm}^3~\mathrm{mol}^{-1}$ is (an average value from Holder, 1980) the partial molar volume of the gas j in the solvent water. In establishing Eq. (9), the activity coefficient of CO_2 in water was in a good approximation neglected and the very good approximations $n_j^{\mathrm{L}} \ll n_{\mathrm{w}}^{\mathrm{L}}$, and $V^{\mathrm{L}} \cong V_{\mathrm{w}}^{\mathrm{L}}$ were applied. $K_{\mathrm{H},j}^{\infty}$ (Pa^{-1}) represents Henry's constant at saturation pressure of the pure solvent, i.e., at infinite dilution of the gaseous component, which as function of temperature is calculated from the following correlation given by Holder (1980):

$$K_{\mathrm{H},j}^{\infty}(T)[\mathrm{Pa}] = \exp\left(-A - \frac{B}{T}\right)$$ (9)

A and B are constants listed in Table 2.

Table 2 Constants for Henry constant calculation, from Holder (1980)

Gas	A	B/K
CO_2	14.283146	-2050.3269
N_2	17.934347	-1933.381
CH_4	15.826277	-1559.0631

3.3.5 Composition of the hydrates phase

After the amounts of substance of gas j in the gas phase n_j^G and in the liquid phase n_j^L have been estimated by the procedures described above, the mole number of the gas j in the hydrate phase n_j^H can be derived from Eq. (1,3,5,6,8), that means the gas encapsulated in the hydrate equals the initial quantity in the feed (eq.3) minus the quantities in the gas at step and the quantity in the liquid. The hydrate composition (molar fraction) can be then calculated with a precision of 0.06 (see annex 1).

4 Thermodynamic Modelling

4.1 Van der Waals and Platteeuw model

The van der Waals and Platteeuw (1959) model describes the hydrate phase by means of statistical thermodynamics based on the following assumptions:

- Each cavity contains at most one guest (gas) molecule

- The interaction between guest and water molecules can be described by a pair potential function of the pair gas-molecule, and the cavity can be treated as perfectly spherical

- The free energy contribution of the water molecules is independent of the modes of occupancy of guest molecules. This assumption means that the gas molecules do not deform cavities

- There is no interaction between the guests molecules in different cavities, gas molecules interact only with the nearest water molecules

From the previous hypotheses, statistical thermodynamics allows for the description of the different parameters of the system and link them to quantities like temperature, volume and chemical potential.

In the case of hydrates, in thermodynamic equilibrium, the equality of chemical potentials of water in the liquid phase and in the hydrate phase can be written. 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:

$$\Delta\mu_{\text{w}}^{\text{H}-\beta} = \Delta\mu_{\text{w}}^{\text{L}-\beta} \tag{10}$$

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

$$\Delta\mu_{\text{w}}^{\text{H}-\beta} = RT\sum_{i} v_i \ln\left(1 - \sum_{j}\theta_j^i\right) \tag{11}$$

In eq. (11) v_i is the number of cavities of type i per mole of water (see Table 1) and θ_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.

The occupancy factor is described by a model based on ideas considering the analogy between the gas adsorption in the 3-dimensional hydrate structure and the 2-dimensional Langmuir adsorption (Sloan, 1998). The assumptions on which the Langmuir adsorption model rests upon are:

- The guest molecule is adsorbed at the surface

- The adsorption energy is independent from the presence of other adsorbed molecules

- The maximum amount of adsorbed gas corresponds to one molecule per site (one molecule par cavity)

- The expression of the occupancy factor θ_j^i is given by:

$$\theta_j^i = \frac{C_j^i f_j(T,P)}{1 + \sum_j C_j^i f_j(T,P)} \qquad (12)$$

Eq. 12 can be rewritten as:

$$\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta} = RT \sum_i \nu_i \ln\left(1 - \sum_j C_j^i f_j(T,P)\right) \qquad (13)$$

Where C_j^i is the Langmuir constant of component j in the cavity i that 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 symmetrical potential:

$$C_j^i = \frac{4\pi}{kT} \int_0^\infty \exp\left(-\frac{w(r)}{kT}\right) r^2 dr \qquad (14)$$

Where w 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 (McKoy, 1963), can be expressed as:

$$w(r) = 2z\varepsilon\left[\frac{\sigma^{12}}{R^{11}r}\left(\delta^{10} + \frac{a}{R}\delta^{11}\right) - \frac{\sigma^6}{R^5 r}\left(\delta^4 + \frac{a}{R}\delta^5\right)\right] \qquad (15)$$

$$\delta^N = \frac{1}{N}\left[\left(1 - \frac{r}{R} - \frac{a}{R}\right)^{-N} - \left(1 + \frac{r}{R} - \frac{a}{R}\right)^{-N}\right] \qquad (16)$$

The gas parameters ε, σ 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. 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).

Comment on the Kihara paramaters

a is a spherical hard-core radius, representing the guest molecule as a spherical hard-sphere. Its value is calculated from results of viscosity measurements (Tee et al, 1996), but it can alternatively be derived from values of the second virial coefficient (Sherwood and Prausnitz, 1964). a is considered as a reliable parameter of general validity that does not need to be fitted again. σ represents the distance from the cavity centre at which the interaction potential w is zero, whereas ε stands for the maximum attractive potential. σ and ε are considered as fitting parameters. In case of gas hydrate equilibria involving a single gas component only the fitting has to be performed at least against equilibrium data of pressure and temperature. If the parameter adjustment is to be carried out on hydrate equilibrium data involving binary gas mixtures, ideally both the gas as well as the hydrate stoichiometry have to be taken into account (Mooijer-van den Heuvel, 2004).

Comment on the geometric description of the cavity

Theoretically, in equation 14, the interaction potential w need to integrated from 0 to infinity, it means that the gas molecule interacts with the overall structure, not only with its first hydration shell (i.e. the water molecules of the cavity in which the gas molecule is encapsulated), but also interacts with other molecules localised away. In fact, John and Holder (1982) have showed that 2nd and 3rd hydration shells contribute significantly to the Langmuir constants which consequence is a change in the Langmuir constant of 1-2 orders of magnitudes (Sparks and Tester, 1992). Also, even with a rigorous integration of the interaction potential over all the hydration shells, the John and Holder model (1982) can only give rigorous results for spherical molecules (such has Kr, Ar, CH4…). John et al (1985) have

so introduced a correction factor to take into account the asymmetry of the encapsulated molecules. All these refinement methods tends to give a physical signification to the interaction potential w and Kihara parameters but results in a time consuming calculation. For this reason, we have retained an integration of the cell potential over the first hydration shell. So, in this work, Kihara parameters σ and ε need to be considered has fitting parameters.

Parrish and Prausnitz (1972) proposed a simplified expression for the Langmuir constant:

$$C_j^i = \frac{A_j^i}{T} \exp\left(\frac{B_j^i}{T}\right)$$

(17)

Where A and B are constants, given in the literature by Munk $et\ al$ (1988). This simplified expression has been introduced to avoid the integration of the interaction potential w which is a rather time consuming calculation. However, a set of two parameters is required for each cavity and one gas, thus a total number of eight parameters is needed to describe a mixture comprised of one gas and two hydrate structures (omitting the structure H that contains three types of cavities). Contrary, by using the Kihara parameters and rigorously integrating the cell potential (eq. 14-16), only three parameters are necessary to simulate both of the structures. Moreover, this way of modelling is based on physical considerations and it is therefore retained in this study.

4.1.1   Determination of $\Delta\mu_w^{L-\beta}$

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 and pressure. The reference conditions are the temperature $T_0 = 273.15$ K and the pressure $P_0 = 0$. 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 β, $\Delta\mu_w^{\varphi-\beta}$, can be written as follows:

$$\Delta\mu_w^{L-\beta} = T\frac{\Delta\mu_w^{L-\beta}\big|_{T^0,P^0}}{T^0} - T\int_{T^0}^{T}\frac{\Delta h_w^{L-\beta}\big|_{P^0}}{T^2}dT + \int_{P^0}^{P}\Delta v_w^{L-\beta}\big|_T dP - RT\ln a_w^L\big|_{T,P} \qquad (18)$$

- The activity of water in the liquid phase, a_w^L, is given as the product of the mole

    fraction of water in the liquid phase, x_w, and the activity coefficient of water in

    that phase, γ_w^L, hence $a_w^L = x_w\gamma_w^L$. In a good approximation, the aqueous phase can

    be regarded as ideal and the activity coefficient therefore be set to a fixed value of

    1, resulting in $a_w^L \cong x_w$. However, in the presence of polar molecules or even salts,

    the system usually shows strong deviations from ideality. In that event, γ_w^L needs

    an appropriate description, as provided e.g. by a simple Pitzer-Debye-Hückel

    model accounting for the long term electrostatic interactions only, or a more

    elaborate model like the eNRTL (Chen et al. 1982, Chen and Evans 1986) or the

    Pitzer (Pitzer 1973, 1980) model to describe also the short range electrostatic

    forces. Nevertheless, in this work there is no need for introducing an additional

    model to describe γ_w^L since the liquid phases encountered in these experiments can

    in very good approximation be treated as pure liquid water. From a practical point

    of view, a_w^L is a second order parameter compared to the three following : $\Delta v_w^{L-\beta}\big|_T$,

    $\Delta h_w^{L-\beta}\big|_{P^0}$ and $\Delta\mu_w^{L-\beta}\big|_{T^0,P^0}$.

- The value of $\Delta v_w^{L-\beta}\big|_T$ is a first order parameter. It has been measured with high

    accuracy by von Stackelberg (1951) from X ray diffraction. Since that data are

    believed to be very reliable, the parameter $\Delta v_w^{L-\beta}\big|_T$ in our model calculations has

    been taken from this source.

18

- The value of $\Delta h_w^{L-\beta}\big|_{P^0}$ is a first order parameter as well. A refinement of the model is given by Sloan (1998, 2008) that takes into account the temperature dependence of $\Delta h_w^{L-\beta}\big|_{P^0}$ using the well-known classical thermodynamic relationship

$$\Delta h_w^{L-\beta}\big|_{P^0} = \Delta h_w^{L-\beta}\big|_{T^0,P^0} + \int_{T^0}^{T} \Delta c_{p,w}^{L-\beta}\big|_{P^0} dT \tag{19}$$

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

$$\Delta c_{p,w}^{L-\beta}\big|_{P^0} = \Delta c_{p,w}^{L-\beta}\big|_{T^0,P^0} + b_{p,w}^{L-\beta}\left(T - T^0\right) \tag{20}$$

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

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

4.1.2 Equilibrium calculations – the adjustment of the model parameters

The phase equilibrium between the water in the hydrate and the water in the liquid phase is described by Eq. (10). For a given set of Kihara parameters ε_j and σ_j, and a given temperature (resp. a given Pressure), the calculated equilibrium pressure P_{calc} (resp. the calculated equilibrium temperature T_{calc}) corresponds the value at which $\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta}$. Then the calculated pressure (resp. the calculated temperature) is compared to the experimental one P_{exp} (resp. T_{exp}) and a deviation function can be defined as:

$$F(\varepsilon_j,\sigma_j) = \sum_{l=1}^{N}\left|\frac{P_{calc}}{P_{exp}} - 1\right| \to \min \text{ (resp. } F(\varepsilon_j,\sigma_j) = \sum_{l=1}^{N}\left|\frac{T_{calc}}{T_{exp}} - 1\right| \to \min \text{)} \tag{21}$$

19

In Eq. (21), the index l assigns the specific data point and the summation is to be performed over all N data of the set. Furthermore, the explicit mentioning of the quantities $\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta,0}$, $\Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\big|_{T}$, $\Delta c_{p,\mathrm{w}}^{\mathrm{L}-\beta,0}$, and $b_{p,\mathrm{w}}^{\mathrm{L}-\beta}$ in the argument list of the functional expression for $\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta,0}$ has been omitted purposely, since these parameters are not the subject and, hence, results of the optimisation, but rather have been set previously to fixed values taken from the literature. Upon introducing the relations given by Eqs. (19) and (20), incorporating the approximation $a_{\mathrm{w}}^{\mathrm{L}} \cong x_{\mathrm{w}}$, and, performing all necessary integrations in the classical thermodynamic relation of Eq. (18), the following equation is derived:

$$
\begin{aligned}
\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta} &= \frac{T}{T^0}\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta,0} + \left(b_{p,\mathrm{w}}^{\mathrm{L}-\beta}T^0 - \Delta c_{p,\mathrm{w}}^{\mathrm{L}-\beta,0}\right)T \ln\frac{T}{T^0} + \frac{1}{2}b_{p,\mathrm{w}}^{\mathrm{L}-\beta}T\left(T^0 - T\right) \\
&+ \left(\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\big|_{T^0,p^0} + \left(b_{p,\mathrm{w}}^{\mathrm{L}-\beta}T^0 - \Delta c_{p,\mathrm{w}}^{\mathrm{L}-\beta}\big|_{T^0,p^0}\right)T^0 - \frac{1}{2}b_{p,\mathrm{w}}^{\mathrm{L}-\beta}T^{0^2}\right)\left(1 - \frac{T}{T^0}\right) \qquad (22) \\
&+ \Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\big|_{T}\left(p - p^0\right) - RT\ln x_{\mathrm{w}}
\end{aligned}
$$

In Eq. (21), the mole fraction of the water in any equilibrium state is derived by using the measured results of the mole numbers of both gases i and k in the liquid phase n_j^{L} and n_k^{L} and the volume of the liquid phase V^{L}, respectively, according to

$$
x_{\mathrm{w}} = \frac{V^{\mathrm{L}}\rho_{\mathrm{w}}^{\circ}}{V^{\mathrm{L}}\rho_{\mathrm{w}}^{\circ} + M_{\mathrm{w}}\left(n_j^{\mathrm{L}} + n_k^{\mathrm{L}}\right)} \qquad (23)
$$

By introducing eq. (14) into the expression of Eq. (13) derived from statistical thermodynamic considerations, the latter appears in the form

$$
\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta} = RT\sum_i \nu_i \ln\left(1 - \frac{4\pi}{kT}\sum_j f_j(T,P,y_j)\int_0^R \exp\left(-\frac{w(r,\varepsilon_j,\sigma_j,a_j)}{kT}\right)r^2 dr\right), \qquad (24)
$$

where $w(r,\varepsilon_j,\sigma_j,a_j)$ is to be replaced by the expressions defined in Eqs. (15) and (16). The accuracy of the model is dependent on the internal parameters of both, eq. (22) and eq. (24),

as well as on the equation of state used to describe the fugacity of the gas phase. In the next part, we will adopt the following nomenclature.

- The reference parameters (or macroscopic parameters such as $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$) will describe the quantities derived directly from classical thermodynamics. Among these parameters a distinction is made between the first order and the second order parameters, respectively, as has been outlined above.

- The Kihara parameters allow for a rigorous calculation of the Langmuir coefficient C_j^i, required in the statistical thermodynamic model for describing the hydrate phase.

Special attention has to be paid when assigning values for $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$ since the corresponding data found in the literature differ strongly from one author to the other, mainly due the difficulties arising when determining these quantities experimentally. The following Table 3 summarizes the values that are allowable and can be found in the open literature as cited by Sloan (1998, 2007). However, in Table 3 we report only the authors who have proposed a complete set of values, for both structures I and II.

Table 6 summarizes the values of the Kihara parameters we obtained following the optimisation method it is explained later. It can be seen that the kihara parameters are effectively dependent on $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$ and we will see later that the parameters from Hand and Tse (1986) seems to be the better choice. But before entering in this discussion, another comment can be done which points the difficulty to compare models from authors. In fact, table 6 gives also the Kihara parameters proposed by Sloan (1998) and Sloan and Koh (2007). In their model, Sloan and Koh have implemented $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$ from Dharmawardhana et al (1980). We can see firstly that values of the Kihara parameters have been modified from 1998 to 2007. Secondly, we can see the values differ from the kihara

parameters we regressed in our work by using also the reference parameters from Dharmawardhana et al (1980). It underlines the difficulty to compare the models between authors because two many points need to be clarified: what are the data on which the models are regressed? What is the method retained in the integration of the cell potential? Do the model have the same reference parameters? So, the comparison between models can not be done by comparing their internal parameters or Kihara parameters, but by comparing the precision of their simulation from a common experimental data base. It is not the purpose of this publication which aims at choosing the best set of $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$ parameters.

Table 3   Mascroscopic parameters of hydrates and Ice from Sloan (1998, 2007)

Structure I		Structure II		
$\Delta\mu_w^{L-\beta,0}$	$\Delta h_w^{1-\beta,0}$	$\Delta\mu_w^{L-\beta,0}$	$\Delta h_w^{1-\beta,0}$	
J/mol	J/mol	J/mol	J/mol	
699	0	820	0	van der Waals and Platteeuw (1959)
1255.2	753	795	837	Child (1964)
1297	1389	937	1025	Dharmawardhana et al (1980)..........model 1(*)
1120	931	1714	1400	John et al (1985) ....model 2(*)
1287	931	1068	764	Handa and Tse (1986)......................model 3(*)
$\Delta h_w^{L-\beta,0} = \Delta h_w^{1-\beta,0} - 6011$, where 6011 is the enthalpy of fusion of Ice (J/mol)				
(*) model refers to the model in which the $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$ reference parameters are implemented as described in the next part of the work.				

The Kihara parameters have been determined by fitting the experimental data (mainly pressure and temperature equilibrium data of pure components) and assuming one type of structure. Therefore, the Kihara parameters are dependent on the values of $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$ which have been retained. In the next part of the work, we will evaluate the performance of three models. Model 1 is the model implemented with $\Delta\mu_w^{L-\beta,0}$ and $\Delta h_w^{L-\beta,0}$ from Dharmawardhana et al (1980), model 2 is implemented with values from John et al (1985) and model 3 is implemented with values from Handa and Tse (1986).

Table 4   Reference properties of hydrates from Sloan (1998, 2007)

	Unit	Structure I	Structure II
$\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta,\,0}$	J mol	$\Delta h_{\mathrm{w}}^{\mathrm{I}-\beta}\big|_{T^0,P^0,\mathrm{SI}}$ -6011	$\Delta h_{\mathrm{w}}^{\mathrm{I}-\beta}\big|_{T^0,P^0,\mathrm{SII}}$ -6011
$\Delta v_{\mathrm{w}}^{\mathrm{L}-\beta}\big|_{T^0}$	10^{-6} m^3/mol	4.5959	4.99644
$\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta,\,0}$	J/(mol K^{-1})	-38.12	-38.12
$b_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}$	J/(mol K^{-2})	0.141	0.141

5   Results and discussion

5.1   Determination of the hydration number of the hydrates at equilibrium

Experimentally, we can determine the volume of water (and so the number of moles of water) which has reacted to form hydrate. This volume is determined from the difference of the tracer concentration of LiNO3 being present in the liquid phase between the beginning and equilibrium (Eq.6).

The quantities of gases which have been incorporated into the lattice structure of the hydrate is calculated from a mass balance Eq. (1). Proceeding in this way we can evaluate the hydration number of the respective hydrate at equilibrium.

Table 5 shows a comparison between the theoretical hydration number (from model 3, see following) and the experimental one, assuming that structure I is formed. The data reveal a good correlation for the pure gas hydrates of CO_2 and CH_4 and a less good one for the case of the CO_2-N_2 gas hydrate.

Table 5   Experimental and theoretical hydration numbers

Experiment	component	P_{eq} /MPa	T_{eq}/K	Experimental Hydration number	Calculated Hydration number(*)
1	CO_2	1.70	275.6	6.35	6.2
2	CO_2	1.45	274.6	6.23	6.2
3	CO_2	1.57	274.8	6.65	6.2
4	CH_4	3.40	275.8	6.29	6.0
5	CH_4	2.83	273.8	6.14	6.1
6	CH_4	2.86	273	6.09	6.0

7	CO$_2$-N$_2$ (15.7%CO$_2$ 84.3% N$_2$)	5.99	273.5	6.1	5.84

(*) calculated from model 3, see following

5.2 Determination of the envelope curves

Qualitative interpretation of the data by visual comparison

Fig. 4 and Fig. 5 show the envelope curve between the gas phase and the hydrate phase obtained from experiments on CO2-CH4 mixtures at temperature 277 K and a CO2-N2 mixture at pressure of around 6 MPa. With regard to the CO2-CH4 mixture at 277 K, we got numerous experimental data covering a wide range of composition. So it is possible to plot an experimental envelope curve. For the binary gas mixture of CO2 and N2, because we have changed our strategy in order to cover a wide range of temperature (in the range 273-281K) and composition (in the range 38-84% CO2), we can report only few points at a constant pressure around the value of 6 MPa (table 8). Figures 4 and 5 also plot the theoretical envelope curve resulting from model 3 that is explained later. First comment is that model and experiment are in a good agreement but the precision of the model is discussed later. Second comment concerns the shape of the envelope curves. CO2-CH4 envelope curve is narrow and CO2-N2 envelope curve is wide. A separation process based on hydrate crystallisation is difficult to envisage in the case of CO2-CH4 but promising in the case of CO2-N2 mixtures.
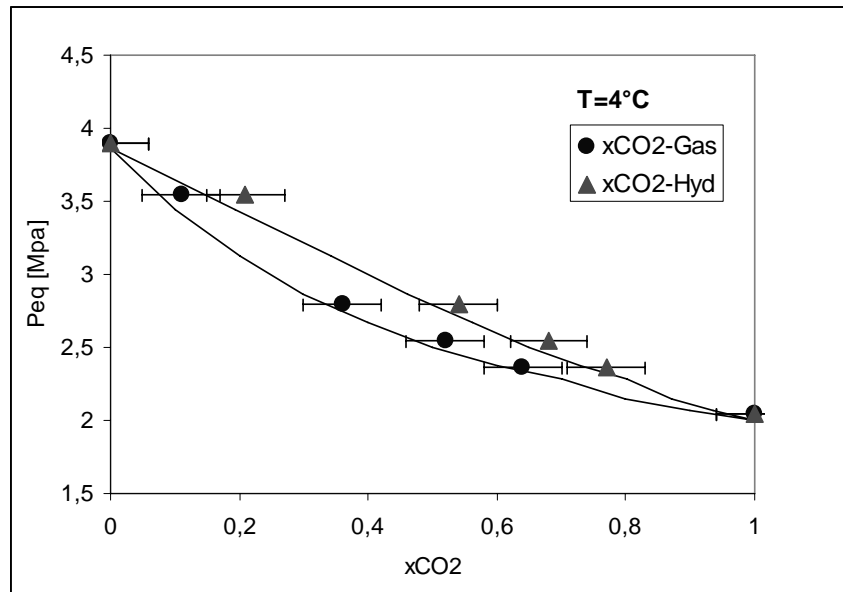
Fig. 4   Gas hydrate phase diagram for CO_2-CH_4 gas mixture at 277 K. x-axis is the molar composition of the gas or hydrate phase (xCO2 + xCH4 = 1) and y-axis is the equilibrium pressure
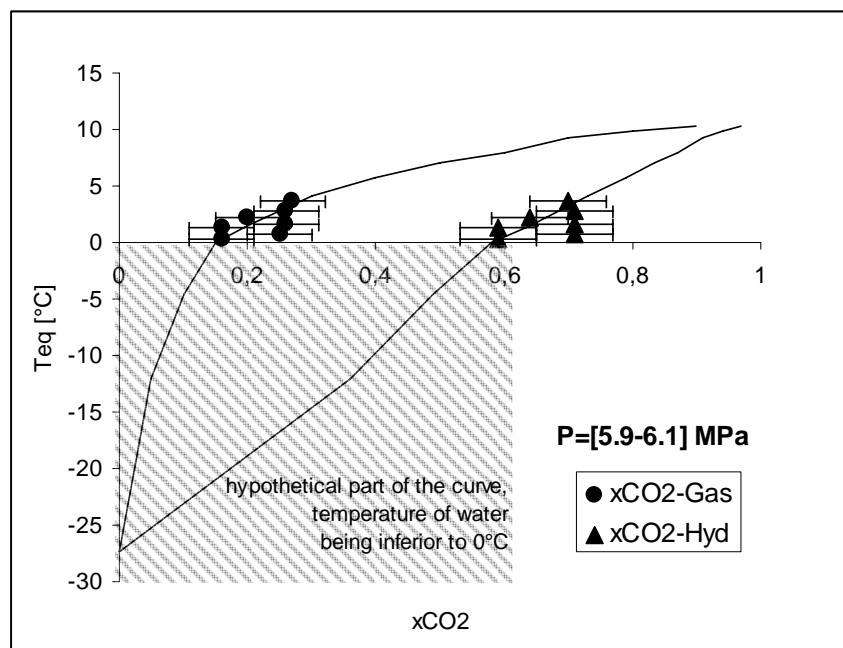
Fig. 5   Gas hydrate phase diagram for CO_2-N_2 gas mixture at pressure of [5.9-6.1 MPa]. x-axis is the molar composition of the gas or hydrate phase (xCO2 + xN2 = 1) and y-axis is the equilibrium temperature.

Procedure to determine the best set of internal parameters

The classical van der Waals and Platteeuw model (1959) is dependent on its internal

parameters: the reference parameters (or macroscopic parameters) are coming from relations

25

obtained from classical thermodynamics (Eq. 19), whereas the Kihara parameters (Ea. 15 and 16) allow for modelling the Langmuir coefficients (Eq. 14).

Our procedure for selecting the best set of internal parameters consists of initially choosing a set of macroscopic parameters from literature (Table 3), followed by an optimisation of the Kihara parameters such that the mean standard deviation between the results calculated by the model equations and selected experimental results is minimized. It results in three different models called model 1, model 2 and model 3. Finally, we retain the best set of parameters (2 macroscopic parameters + 3 optimized Kihara parameters) which is the one belonging to the lower mean standard deviation. In detail, the following procedure is applied:

Stage 1: determination of the best set of macroscopic parameters

1) Choice of a set of macroscopic parameters from Table 3.

2) Under the assumption of a SI and SII structure, respectively, retrieving the best Kihara parameters by adjusting ε, σ and a to minimize the mean standard deviation between the experimental data and the corresponding data calculated from the model (Tables 7, 8 and 9)

   i. Calculation of the mean standard deviation for the pressure and temperature equilibrium data in case of the systems containing only a single gaseous component (CO_2, CH_4 and N_2) (data from the literature)

   ii. Calculation of the mean standard deviation of pressure, temperature and hydrate composition from our experimental data for the CO_2-CH_4 and CO_2-N_2 mixtures

3) Validation of the set of optimised parameters with the experimental results from Jhaveri and Robinson (1965) who give a complete set of data on the equilibrium pressure and hydrate composition of the binary CH_4-N_2 hydrate (Table 10).

Stage 2: following stage 1, we got three sets of optimised Kihara parameters, based on three sets of macroscopic parameters following the values given by Dharmawardhana et al. (1980), John et al. (1985) and Handa and Tse (1986) in Table 3. Subsequently, each set of parameters (2 macroscopic parameters + 3 Kihara parameters) is implemented in the van der Waals and Platteeuw model (1959) and we compare the experimental results with data available in the literature. We found two publications, one of Seo et al. (2000) in which both binary gas mixtures, the CO_2-N_2 as well as the CO_2-CH_4 mixture, are studied, and a work of Kang et al. (2000) in which the binary mixture CO_2-N_2 is studied (Tables 11, 13, and 14, respectively).
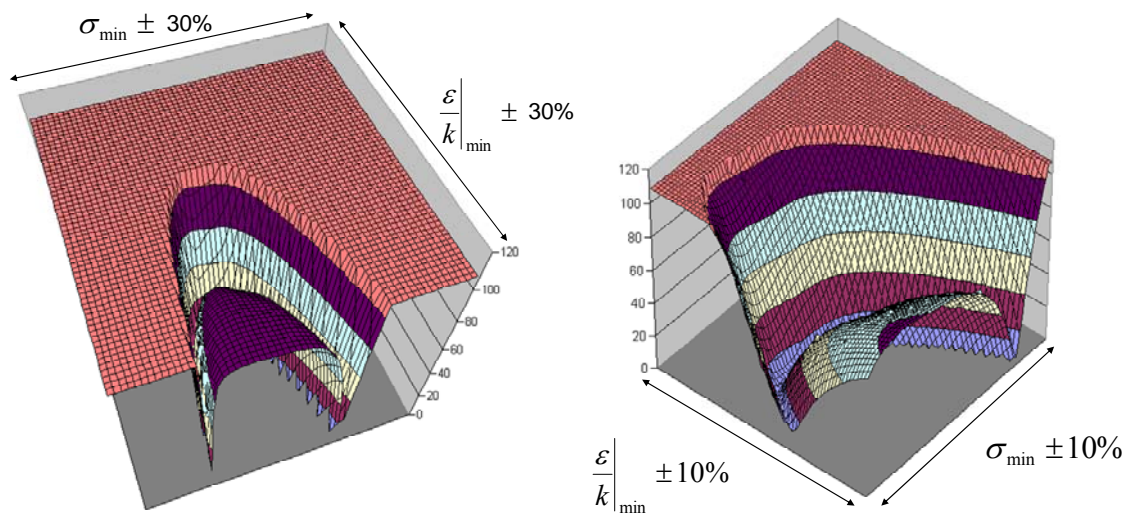
Fig. 6 Typical shape of the deviation (average deviation of the equilibrium pressure) between the model and the experimental results as a function of the Kihara parameters. x and y axes correspond respectively to kihara parameters σ and ε which are varied plus or minus 10% around their best value. The best set of value σ and ε is the one that minimises the objective function F (in equation 21)

Special comment on step 2 of stage 1: From a numerical point of view, the determination of the best set of Kihara parameters (given a set of macroscopic parameters) is time consuming. In fact, in Fig. 6 the typical shape of a surface plot of the objective function, giving the deviation between the modelled data to the experimental data, versus the Kihara parameters is shown. In this example, the experimental results concern the hydrate equilibrium corresponding to pure CO_2 (Adisasmito et al., 1991, reference (b) in Table 7) and the model is

implemented with macroscopic parameters from Handa and Tse (see Table 3). The average deviation is calculated from the 9 experimental equilibrium pressures and the 9 calculated pressures (called ADi in Table 7). We varied ε/k and σ around its best value (see Table 7) in the range plus or minus 10%. It can be noticed from Fig. 6 that the minimum is localised in a deep but flat bottom valley on which the algorithm of minimisation need to move slowly.

Stages 1.1 and 1.2: Choice of a set of macroscopic parameters from Table 3 and determination of the best set of Kihara parameters to fit with experimental results

Table 8 and Table 9 give the comparison between our experimental results and the results of the model using the optimised set of Kihara parameters with the three sets of macroscopic parameters (Table 3) being implemented in the model from Dharmawardhana et al. (1980), John et al. (1985) and Handa and Tse (1986). For each set of macroscopic parameters, we have optimised the Kihara parameters, and the results are given in

Table 6. Tables 7 and 8 present the experimental points (pressure, temperature, gas composition, and hydrate composition) on the left part. The mid-column indicates the structure that is presented as the most stable one from the model. The right part of the table shows the results of the simulation for the best set of reference parameters (which turns out to be the parameters from Handa and Tse (1986): we present the calculated values of pressure and composition, and additionally the deviation between calculated and measured results. At the bottom of the table the average deviation from the three sets of macroscopic parameters from Dharmawardhana et al. (1980), John et al. (1985) and Handa and Tse (1986) is presented. The models have been run with an optimised set of Kihara parameters which are recapitulated   in

Table 6.

Table 7 shows the comparison of models with experiments on (CO_2-CH_4) mixtures (this study). All the models reveal to be very efficient, both with regard to the estimation of the equilibrium pressure as well as the hydrate composition. At that level of the presentation, it is difficult to underline/identify the best model description. The best model description seems to be the one using Kihara parameters that have been fitted after implementation of the reference properties from Handa and Tse (1986). The average deviation for this case amounts to 3% for the calculation of the equilibrium pressure, and a remarkable good evaluation of the gas composition, both for the CO_2 (deviation of 0.6%) and the CH_4 system (deviation of 1.25%), has been attained. The situation changes completely if we take a look at the CO_2-N_2 mixture. The Kihara parameters regressed on the data of the hydrate equilibrium involving N_2 as a single gas under the assumption of a SII structure (see Table 7) is implemented in the model. The corresponding results are compared with our experimental results. Using the reference properties from Dharmawardhana et al. (1980) or John et al. (1985), the model fails in simulating the experimental data. With the reference properties from Handa and Tse (1986) as given in Table 3, and optimised Kihara parameters from

Table 6 (this study), we observe a good agreement between the model and the experiments, with respect to the evaluation of both, the equilibrium pressure (average deviation of 8.1%) as well as the hydrate composition. For the latter we observe an excellent evaluation of the CO_2 composition (average deviation of 4.4%) and at least a reasonable evaluation of the N_2 composition (average deviation of 10.4%).

Table 6   Kihara parameters regressed from experimental results of this study, and Kihara parameters from litterature

	Kihara parameters regressed from experimental results of this study and implemented in model 1,2,3 with macroscopic parameters from table 3 (1)Dharmawardhana et al, 1980 - (2) John et al, 1985 – (3) Handa an Tse, 1986								
	CO_2			CH_4			N_2		
	$\dfrac{\varepsilon}{k}$	σ	a	$\dfrac{\varepsilon}{k}$	σ	a	$\dfrac{\varepsilon}{k}$	σ	a
Model 1	170.00	2.9855	0.6805	157.85	3.1439	0.3834	126.98	3.0882	0.3526
Model 2	164.56	2.9824	0.6805	154.47	3.1110	0.3834	166.38	3.0978	0.3526
Model 3	171.41	2.9830	0.6805	158.71	3.1503	0.3834	138.22	3.0993	0.3526
	Kihara parameters from literature								
Sloan, 1998	168.77	2.9818	0.6805	154.54	3.1650	0.3834	125.15	3.0124	0.3526
Sloan, 2007	175..405	2.97638	0.6805	155.593	3.14393	0.3834	127.426	3.13512	0.3526

Stage 1.3: validation of the best set of parameters on experimental results from the literature for the N_2-CH_4 equilibrium

The literature presents a large amount of experimental data giving the equilibrium pressure as a function of the temperature and gas composition, especially for pure gases and binary components. However, the literature is poor in presenting complete sets of equilibrium data: pressure, temperature, gas, as well as hydrate composition. Fortunately, the work of Jhaveri and Robinson (1965) presents such data for the system containing the binary gas mixture N_2-CH_4. As we have presented our own experimental results for the CO_2-N_2 and CO_2-CH_4 mixtures, the data of Jhaveri and Robinson (1965) are particularly interesting because they allow for "closing the composition triangle" with the data on the N_2-CH_4 mixture. The comparison between the models is presented in Table 10. The best model continues to be the model 3 (i.e., the Kihara parameters fitted in this work in combination with the reference properties from Handa and Tse (1986)) with a reasonable average deviation of about 13% for the evaluation of the equilibrium pressure, and a deviation of about 10% for the evaluation of the hydrate composition.

So, at this intermediate level of the discussion, we can asses that we dispose of a reliable model (model 3) to predict both binary mixtures and pure gas equilibrium of gases composed from the CO_2, CH_4, N_2 elements. Nevertheless, we do not have data to validate the model 3 for the ternary system $CO_2 + CH_4 + N_2$.

Table 7 Experimental data and comparison to models for CO_2 and CH_4 and CO_2-CH_4 gas hydrates

	Experiment						Structure	Simulation					
			Gas Molar fraction		Hydrate Molar fraction			Pressure		Hydrate Molar fraction ± 0.06			
	T	P_{eq}						P_{eq}					
	°C	MPa	CO_2	CH_4	CO_2	CH_4		MPa	%D3	CO_2	%D3	CH_4	%D3
(a)	4.00	2.04	1.00	0.00	1.00	0.00	SI	2.00	1.92	1.00	0.00	0.00	0.00
(a)	4.00	2.36	0.64	0.36	0.77	0.23	SI	2.32	1.72	0.76	1.16	0.24	3.83
(a)	4.00	2.55	0.52	0.48	0.68	0.32	SI	2.47	3.15	0.67	1.09	0.33	2.28
(a)	4.00	2.80	0.36	0.64	0.54	0.46	SI	2.74	2.18	0.53	1.17	0.47	1.34
(a)	4.00	3.55	0.11	0.89	0.21	0.79	SI	3.39	4.56	0.21	0.20	0.79	0.06
(a)	4.00	3.90	0.00	1.00	0.00	1.00	SI	3.88	0.59	0.00	0.00	1.00	0.00
(b)	0.15	1.42	1	0	1	0	SI	1.27	10.25	1		0	
(b)	2.35	1.63	1	0	1	0	SI	1.64	0.83	1		0	
(b)	3.65	1.90	1	0	1	0	SI	1.92	0.93	1		0	
(b)	4.45	2.11	1	0	1	0	SI	2.11	0.17	1		0	
(b)	5.95	2.55	1	0	1	0	SI	2.55	0.04	1		0	
(b)	7.45	3.12	1	0	1	0	SI	3.11	0.29	1		0	
(b)	8.35	3.51	1	0	1	0	SI	3.53	0.70	1		0	
(b)	8.95	3.81	1	0	1	0	SI	3.87	1.50	1		0	
(b)	9.75	4.37	1	0	1	0	SI	4.37	0.01	1		0	
(c)	0.25	2.68	0	1	0	1	SI	2.63	1.94	0		1	
(c)	1.45	3.05	0	1	0	1	SI	2.97	2.67	0		1	
(c)	3.55	3.72	0	1	0	1	SI	3.70	0.62	0		1	
(c)	5.15	4.39	0	1	0	1	SI	4.37	0.46	0		1	
(c)	6.45	5.02	0	1	0	1	SI	5.05	0.61	0		1	
(c)	7.75	5.77	0	1	0	1	SI	5.83	0.97	0		1	
(c)	9.15	6.65	0	1	0	1	SI	6.90	3.80	0		1	
(c)	10.45	7.59	0	1	0	1	SI	8.11	6.80	0		1	
(c)	11.55	8.55	0	1	0	1	SI	9.34	9.25	0		1	
(c)	12.55	9.17	0	1	0	1	SI	10.73	17.06	0		1	
(c)	13.25	10.57	0	1	0	1	SI	11.87	12.34	0		1	
AD1									2.22		1.15		2.46
AD2									3.16		1.67		3.14
AD3									3.04		0.60		1.25

For each line, an individual deviation called %D3 is evaluated between experimental data and model implemented with reference properties from (3)
ADi is an average deviation referring to models i=1..3 in which reference properties are from
 (1)Dharmawardhana et al (1980) - (2) John et al (1985) – (3) Handa and Tse (1986)

(a) experimental equilibrium data from this study
(b) and (c) experimental equilibrium data from Adisasmito et al, 1991

Table 8 Experimental data and comparison to models for CO_2- N_2 gas hydrates

	Experiment						Structure	Simulation					
	°C	MPa	Gas Molar fraction		Hydrate Molar fraction			Pressure MPa		Hydrate Molar fraction ± 0.06			
	T	Peq	CO_2	N_2	CO_2	N_2		Peq	%D3	CO_2	%D3	N_2	%D3
(a)	0.25	6.10	0.16	0.84	0.66	0.34	SI	5.79	5.01	0.59	10.20	0.41	19.62
(a)	1.35	6.20	0.16	0.84	0.66	0.34	SI	6.49	4.70	0.59	9.86	0.41	18.89
(a)	2.25	6.40	0.19	0.82	0.66	0.34	SI	6.73	5.13	0.62	6.08	0.38	11.60
(a)	3.35	6.60	0.20	0.80	0.58	0.42	SI	7.41	12.26	0.63	7.13	0.37	10.02
(a)	0.75	5.90	0.25	0.75	0.75	0.25	SI	4.38	25.74	0.71	5.42	0.29	16.43
(a)	1.55	5.90	0.26	0.75	0.73	0.27	SI	4.82	18.29	0.71	3.08	0.29	8.33
(a)	2.85	5.90	0.26	0.74	0.70	0.30	SI	5.57	5.54	0.71	0.17	0.29	0.41
(a)	3.75	6.00	0.27	0.74	0.70	0.30	SI	6.29	4.76	0.70	0.58	0.30	1.38
(a)	4.65	6.30	0.29	0.71	0.67	0.33	SI	6.62	5.04	0.72	6.59	0.28	13.43
(a)	4.95	6.40	0.30	0.71	0.69	0.31	SI	6.84	6.87	0.72	3.58	0.28	8.01
(a)	5.25	6.40	0.30	0.71	0.72	0.29	SI	7.17	12.06	0.71	0.38	0.29	0.96
(a)	5.45	6.50	0.30	0.70	0.70	0.31	SI	7.27	11.80	0.72	2.96	0.28	6.74
(a)	2.25	6.10	0.20	0.80	0.67	0.33	SI	6.29	3.04	0.64	4.25	0.36	8.64
(a)	2.85	6.20	0.22	0.78	0.65	0.35	SI	6.44	3.93	0.66	1.26	0.34	2.33
(a)	6.95	5.30	0.56	0.44	0.85	0.16	SI	5.17	2.47	0.87	2.40	0.13	13.08
(a)	7.95	5.60	0.59	0.42	0.82	0.18	SI	5.79	3.47	0.87	6.14	0.13	27.80
AD1									39.18		10.31		25.20
AD2									70.81		53.67		127.3
AD3									8.13		4.38		10.38

For each line, an individual deviation called %D3 is evaluated between experimental data and model implemented with reference properties from (3)
ADi is an average deviation referring to models i=1..3 in which reference properties are from
 (1)Dharmawardhana et al (1980) - (2) John et al (1985) – (3) Handa and Tse (1986)
(a) experimental equilibrium data from this study

Table 9   Experimental data from literature and comparison with model for N_2 gas hydrates

Experiment			Simulations					
			Model 3		Model 2		Model 1	
			Simulated Pressure		Simulated Pressure		Simulated Pressure	
	°C	MPa	MPa	%D3	MPa	%D2	MPa	%D1
	T	Peq						
(d)	0.05	16.01	13.17	17.72	13.62	14.96	13.63	14.86
(d)	0.05	16.31	13.17	19.24	13.62	16.52	13.63	16.42
(d)	0.25	16.62	13.49	20.74	13.93	16.17	13.93	16.17
(d)	0.85	17.53	14.50	23.05	14.95	14.74	14.98	14.56
(d)	1.05	17.73	14.85	18.21	15.29	13.74	15.33	13.56
(d)	1.65	19.15	15.99	22.45	16.43	14.18	16.50	13.81
(d)	1.65	19.25	15.99	16.93	16.43	14.63	16.50	14.26
(d)	2.05	19.66	16.78	18.67	17.23	12.38	17.32	11.90
(d)	2.45	20.67	17.67	18.81	18.11	12.38	18.18	12.07
(d)	2.65	21.58	18.11	18.13	18.56	14.02	18.65	13.58
(d)	3.05	22.39	19.06	19.11	19.25	14.02	19.62	12.39
(d)	3.45	23.1	20.06	17.48	20.49	11.31	20.61	10.76
(d)	4.05	24.83	21.66	19.21	22.10	10.99	22.26	10.35
(d)	5.05	27.36	24.70	20.84	25.11	8.23	25.32	7.47
(d)	5.05	27.97	24.70	11.70	25.11	10.23	25.32	9.49
(d)	5.45	28.27	26.06	12.64	26.44	6.48	26.66	5.69
(d)	6.05	29.89	28.24	12.82	28.56	4.45	28.85	3.49
(d)	6.05	30.3	28.24	6.78	28.56	5.74	28.85	4.80
(d)	7.05	33.94	32.33	16.78	32.55	4.09	32.42	4.47
(d)	8.05	37.49	37.05	13.77	36.98	1.35	37.49	0.00
(d)	8.45	38.61	39.14	4.05	39.26	1.69	39.64	2.68
(d)	9.05	41.44	42.49	5.56	41.54	0.25	42.94	3.61
(d)	10.05	45.9	48.76	7.42	48.64	5.96	49.14	7.06
(d)	11.05	50.66	55.98	3.75	55.60	9.76	56.17	10.88
(d)	11.45	52.29	59.15	7.06	57.76	10.45	59.28	13.36
(d)	12.05	55.43	64.28	6.71	63.58	14.71	64.21	15.85
(d)	13.05	61.4	73.71	4.69	71.94	17.17	72.95	18.82
(d)	14.05	67.79	84.73	8.74	83.09	22.56	83.85	23.69
(d)	14.65	71.23	92.08	18.96	90.18	26.60	90.69	27.31
(d)	15.25	74.58	100.1	23.46	98.29	31.78	98.54	32.12
(d)	16.05	81.47	112.0	22.82	109.4	34.32	109.6	34.63
(d)	17.05	89.37	128.7	25.28	126.1	41.15	125.4	40.59
(d)	17.45	92.21	136.7	39.55	133.7	45.05	132.3	43.95
(d)	17.85	95.86	144.8	42.70	140.8	46.92	140.3	46.40
AD1								15.62
AD2						15.74		
AD3				16.64				

For each line, an individual deviation called %D3 is evaluated between
experimental data and model implemented with reference properties from
(3)
ADi is an average deviation referring to models i=1..3 in which reference
properties are from
(1) Dharmawardhana et al. (1980) -(2) John et al. (1985) – (3) Handa and
Tse (1986)
(d) experimental data from van Cleeff and Diepen (1960)

Table 10 Experimental data from Jhaveri and Robinson (1986) in comparison with results obtained from model calculations for N_2-CH_4 gas hydrate

	Experiment						Structure	Simulation					
			Gas Molar fraction		Hydrate Molar fraction			Pressure		Hydrate Molar fraction			
	T	P_{eq}						P_{eq}					
	°C	MPa	N_2	CH_4	N_2	CH_4		MPa	%D3	N_2	%D3	CH_4	%D3
(e)	0.05	2.64	0.00	1.00	0.00	1.00	SI	2.58	2.40	0.00			
(e)	0.05	3.62	0.16	0.84	0.07	0.94	SI	2.99	17.40	0.04	33.01	0.96	2.30
(e)	0.05	4.31	0.31	0.69	0.10	0.90	SI	3.51	18.45	0.10	0.81	0.90	0.09
(e)	0.05	5.35	0.53	0.47	0.20	0.80	SI	4.73	11.67	0.21	6.97	0.79	1.74
(e)	0.05	6.55	0.65	0.36	0.35	0.65	SI	5.75	12.26	0.31	12.52	0.69	6.74
(e)	0.05	7.75	0.73	0.28	0.43	0.58	SI	6.74	12.97	0.39	7.79	0.61	5.76
(e)	0.05	10.64	0.82	0.19	0.62	0.38	SI	8.37	21.36	0.52	15.94	0.48	26.01
(e)	0.05	11.65	0.88	0.12	0.71	0.29	SI	10.07	13.57	0.65	8.89	0.35	21.77
(e)	0.05	12.77	0.90	0.10	0.77	0.24	SII	10.61	16.93	0.77	1.00	0.23	3.24
(e)	4.25	3.86	0.00	1.00	0.00	1.00	SI	3.98	3.15	0.00			
(e)	4.25	5.20	0.44	0.56	0.18	0.82	SI	6.59	26.66	0.17	5.87	0.83	1.29
(e)	4.25	8.11	0.63	0.37	0.31	0.69	SI	9.07	11.86	0.31	0.19	0.69	0.08
(e)	4.25	10.34	0.74	0.26	0.47	0.53	SI	11.50	11.24	0.43	7.72	0.57	6.85
(e)	4.25	12.06	0.78	0.22	0.56	0.44	SI	12.70	5.28	0.49	12.48	0.51	15.89
(e)	4.25	13.32	0.93	0.07	0.81	0.19	SII	18.90	41.92	0.84	3.37	0.16	14.38
(e)	4.25	14.59	0.94	0.06	0.86	0.14	SII	19.51	33.69	0.87	0.86	0.13	5.26
(e)	4.25	16.21	1.00	0.00	1.00	0.00	SII	22.23	37.13	1.00			
(e)	6.65	5.14	0.00	1.00	0.00	1.00	SI	5.17	0.57	0.00			
(e)	6.65	7.14	0.35	0.65	0.09	0.91	SI	7.69	7.76	0.13	40.58	0.87	4.06
(e)	6.65	8.37	0.46	0.54	0.22	0.78	SI	9.06	8.29	0.19	15.14	0.81	4.37
(e)	6.65	15.55	0.75	0.25	0.55	0.45	SI	16.16	3.95	0.46	15.68	0.54	19.16
(e)	6.65	20.67	0.84	0.16	0.68	0.32	SI	20.58	0.43	0.61	10.86	0.39	23.07
(e)	6.65	25.23	0.91	0.09	0.80	0.20	SII	25.62	1.53	0.82	2.83	0.18	11.47
(e)	6.65	32.42	1.00	0.00	1.00	0.00	SII	30.62	5.55	1.00			
AD1									27.50		20.04		23.67
AD2									66.01		123.7		61.82
AD3									13.58		10.66		9.13

For each line, an individual deviation called %D3 is evaluated between experimental data and model implemented with reference properties from (3)
ADi is an average deviation referring to models i=1..3 in which reference properties are from
(1) Dharmawardhana et al. (1980), (2) John et al. (1985), (3) Handa and Tse (1986)
(e) experimental data from Jhaveri and Robinson (1986)

Stage 2: Comparison with other results from the literature

In this part of the work, we are going to compare our experimental results with results from the literature. At this stage we have optimised, by means of our experimental data, the parameters of the van der Waals and Platteeuw model (1959) based on using the macroscopic parameters form Handa and Tse (Table 3) and the Kihara parameters from

Table 6. Now, this optimised model is compared with experimental data found in the literature for the systems composed of the binary gas mixtures CO_2-N_2 and CO_2-CH_4. We have found two publications dealing with these systems, one of Seo et al. (2000) in which both, the system containing the binary mixture CO_2-N_2 as well as the one containing CO_2-CH_4 are studied, and an article of Kang et al. (2000) is which equilibrium data corresponding to the binary mixture CO_2-N_2 are reported (Tables 11, 12, and 13). For the CO_2-N_2 gas mixture, none of the models is able to predict both, the equilibrium pressure as well as the hydrate composition, of the experimental results from Seo et al. (2000,

Table 11) and Kang et al. (2000, Table 12) with sufficient accuracy. Whereas model 2 is never efficient, a valuable evaluation of the equilibrium pressure and the CO_2 composition is provided by models 1 and 3, the model 1 of which being the more accurate one. The equilibrium pressure is evaluated by model 1 with an accuracy of 6.61% and 7.19%, respectively, for the results of Seo et al. and Kang et al.; in contrast, the accuracy of model 3 amounts to 13.75% and 11.62%, respectively. The CO_2 composition is estimated by means of model 1 with an accuracy of 9.25 and 8.65%, respectively, for the results of Seo et al. and Kang et al., whereas the accuracy of model 3 is found to be 5.81 and 16.95%, respectively. The N_2 composition is determined by model 1 to within ±19.64 and ±18.96%, respectively, for the results of Seo et al. and Kang et al., whereas the accuracy of model 3 is respectively 55.16 and 56.40%.

Two intermediate comments can be done.

The first comment concerns the model 3. We need to recall that it allows to feet better than model 1 and 2 with our data published in this paper (Table 7 and 8 for the mixture CO2-N2 and CO2-CH4) and but also with literature data for CH4-N2 mixture (Table 10). Model 3 is also valuable in the estimation of pure gas equilibrium. At this step of the work, the model 3 seems self-consistent. But, model 3 fails in estimating the equilibrium of CO2-N2 mixtures from other sources (Table 11 and 12). A definitive conclusion is our experimental results differ from literature.

A second comment concerns model 1, which is less efficient than model 3 on our experimental results (CO2-N2 and CO2-CH4 equilibrium data), but also less efficient for CH4-N2 equilibrium data from literature. But this model 1 becomes the more efficient for CO2-N2 mixtures from literature data (Tables 11 and 12). So, the model 1 is partially self-

consistent because it models data from literatures for CO2-N2 mixtures, but not CH4-N2.from

literature (Table 10).

For the CO_2-CH_4 gas mixture (experimental results of Seo et al. (2000), Table 13), only the

equilibrium pressure can be regarded as being well evaluated by model 3 (average deviation

of 7.19%) and model 1 (average deviation of 10.11%). The CO_2 composition is in none of the

calculations evaluated well. For CO2 composition in the hydrate phase, an average deviation

of around 35% can be achieved by each of the models. In contrast, the correlation of the mole

fraction of N_2 in the hydrate phase fails completely, reflected by an average deviation of some

hundred percents for this quantity by each of the models.

Table 11   **Experimental data from Seo et al (2000) and comparison to models for**

CO$_2$-N$_2$ gas hydrate

	Experiment						Structure	Simulation					
	°C	MPa	Gas Molar fraction		Hydrate Molar fraction			Pressure MPa		Hydrate Molar fraction			
	T	Peq	CO$_2$	N$_2$	CO$_2$	N$_2$		Peq	%D3	CO$_2$	%D3	N$_2$	%D
(f)	0.85	1.39	1.00	0.00	1.00	0.00	SI	1.38	1.19	1.00		0.00	
(f)	0.85	1.77	0.82	0.18	0.99	0.02	SI	1.65	6.48	0.97	2.01	0.03	132.1
(f)	0.85	2.35	0.60	0.40	0.95	0.05	SI	2.18	7.19	0.91	4.90	0.09	96.47
(f)	0.85	2.84	0.50	0.50	0.93	0.07	SI	2.54	10.58	0.87	6.48	0.13	86.29
(f)	0.85	3.46	0.40	0.60	0.90	0.10	SI	3.09	10.83	0.82	9.02	0.18	81.27
(f)	0.85	7.24	0.21	0.79	0.58	0.42	SI	5.18	28.44	0.66	12.67	0.34	17.76
(f)	0.85	11.20	0.12	0.88	0.34	0.66	SI	7.60	32.15	0.50	46.42	0.50	24.19
(f)	0.85	14.93	0.05	0.95	0.18	0.82	SI	11.45	23.32	0.29	59.15	0.71	12.92
(f)	0.85	17.93	0.00	1.00	0.00	1.00	SII	14.50	19.10	0.00		1.00	
(f)	3.85	1.95	1.00	0.00	1.00	0.00	SI	1.97	0.62	1.00		0.00	
(f)	3.85	2.60	0.85	0.15	0.98	0.02	SI	2.29	11.86	0.97	0.98	0.03	43.87
(f)	3.85	3.38	0.59	0.41	0.95	0.05	SI	3.22	4.71	0.89	5.68	0.11	98.59
(f)	3.85	5.23	0.39	0.61	0.89	0.11	SI	4.61	11.96	0.80	10.09	0.20	78.98
(f)	3.85	11.98	0.18	0.82	0.54	0.46	SI	8.77	26.79	0.58	7.95	0.42	9.34
(f)	3.85	15.50	0.12	0.88	0.35	0.65	SI	11.65	24.82	0.46	30.72	0.54	16.73
(f)	3.85	19.17	0.07	0.93	0.19	0.81	SI	15.58	18.75	0.31	61.76	0.69	14.75
(f)	3.85	24.04	0.00	1.00	0.00	1.00	SII	21.12	12.15	0.00		1.00	
(f)	6.85	2.80	1.00	0.00	1.00	0.00	SI	2.87	2.45	1.00		0.00	
(f)	6.85	3.60	0.83	0.18	0.98	0.02	SI	3.48	3.36	0.96	1.88	0.04	78.27
(f)	6.85	4.23	0.70	0.30	0.96	0.04	SI	4.09	3.32	0.92	4.25	0.08	105.2
(f)	6.85	5.07	0.59	0.41	0.94	0.06	SI	4.82	4.88	0.88	6.70	0.12	111.2
(f)	6.85	8.28	0.39	0.61	0.86	0.14	SI	7.09	14.29	0.77	10.51	0.23	66.86
(f)	6.85	14.97	0.25	0.75	0.64	0.36	SI	10.80	27.89	0.64	0.18	0.36	0.31
(f)	6.85	20.75	0.17	0.83	0.45	0.55	SI	14.80	28.67	0.52	15.82	0.48	12.95
(f)	6.85	26.69	0.09	0.91	0.22	0.78	SI	21.66	18.85	0.34	53.73	0.66	15.30
(f)	6.85	32.31	0.00	1.00	0.00	1.00	SII	31.41	2.78	0.00		1.00	
AD1									6.61		9.25		19.64
AD2									61.64		43.31		367.9
AD3									13.75		17.54		55.16

For each line, an individual deviation called %D3 is evaluated between experimental data and model
implemented with reference properties from (3)
ADi is an average deviation referring to models i=1..3 in which reference properties are from
 (1)Dharmawardhana et al. (1980) - (2) John et al. (1985) – (3) Handa and Tse (1986)
(f) experimental data from from Seo et al. (2000)

Table 12 Experimental data from Kang et al. (2001) and comparison to models for CO_2-N_2 gas hydrate

	Experiment						Structure	Simulation					
			Gas Molar fraction		Hydrate Molar fraction			Pressure		Hydrate			
	°C	MPa						MPa		Molar fraction			
	T	Peq	CO2	N2	CO2	N2		Peq	%D3	CO2	%D3	N2	%D
(g)	0.85	1.36	1.00	0.00	1.00	0.00	SI	1.38	1.06	1.00		0.00	
(g)	0.85	1.73	0.82	0.18	0.99	0.02	SI	1.65	4.31	0.97	2.01	0.03	132.06
(g)	0.85	2.30	0.60	0.40	0.95	0.05	SI	2.18	4.88	0.91	4.71	0.09	89.48
(g)	0.85	2.77	0.50	0.50	0.93	0.07	SI	2.54	8.51	0.87	6.48	0.13	86.29
(g)	0.85	3.48	0.40	0.60	0.90	0.10	SI	3.09	11.34	0.82	9.02	0.18	81.27
(g)	0.85	7.07	0.21	0.79	0.58	0.42	SI	5.18	26.79	0.66	12.67	0.34	17.76
(g)	0.85	10.95	0.12	0.88	0.34	0.66	SI	7.60	30.59	0.50	46.42	0.50	24.19
(g)	0.85	14.59	0.05	0.95	0.18	0.82	SI	11.45	21.56	0.29	59.15	0.71	12.92
(g)	0.85	17.52	0.00	1.00	0.00	1.00	SII	14.50	17.24	0.00		1.00	
(g)	3.85	1.91	1.00	0.00	1.00	0.00	SI	1.97	2.89	1.00		0.00	
(g)	3.85	2.54	0.85	0.15	0.98	0.02	SI	2.29	9.78	0.97	1.16	0.03	56.81
(g)	3.85	3.30	0.57	0.43	0.95	0.05	SI	3.32	0.51	0.88	6.48	0.12	112.36
(g)	3.85	5.12	0.39	0.61	0.89	0.11	SI	4.61	10.02	0.80	10.09	0.20	78.98
(g)	3.85	11.71	0.18	0.82	0.54	0.46	SI	8.77	25.10	0.58	7.95	0.42	9.34
(g)	3.85	15.15	0.12	0.88	0.35	0.65	SI	11.40	24.76	0.47	33.30	0.53	18.14
(g)	3.85	18.74	0.07	0.93	0.19	0.81	SI	15.58	16.87	0.31	61.76	0.69	14.75
(g)	3.85	23.50	0.00	1.00	0.00	1.00	SII	21.12	10.13	0.00		1.00	
(g)	3.85	1.91	1.00	0.00	1.00	0.00	SI	1.97	2.89	1.00		0.00	
(g)	3.85	2.54	0.85	0.15	0.98	0.02	SI	2.29	9.78	0.97	1.16	0.03	56.81
(g)	6.85	2.74	1.00	0.00	1.00	0.00	SI	2.87	4.73	1.00		0.00	
(g)	6.85	3.52	0.83	0.17	0.98	0.02	SI	3.46	1.72	0.96	2.10	0.04	102.7
(g)	6.85	4.14	0.70	0.30	0.96	0.04	SI	4.09	1.15	0.92	4.13	0.08	99.01
(g)	6.85	4.95	0.59	0.41	0.94	0.06	SI	4.82	2.61	0.88	6.38	0.12	99.94
(g)	6.85	8.09	0.39	0.61	0.86	0.14	SI	7.09	12.33	0.77	10.09	0.23	61.97
(g)	6.85	14.64	0.25	0.75	0.64	0.36	SI	10.80	26.25	0.64	0.18	0.36	0.31
(g)	6.85	20.29	0.17	0.83	0.45	0.55	SI	14.80	27.04	0.52	15.82	0.48	12.95
(g)	6.85	26.09	0.09	0.91	0.22	0.78	SI	21.66	16.99	0.34	54.91	0.66	15.49
(g)	6.85	31.58	0.00	1.00	0.00	1.00	SII	31.41	0.54	0.00		1.00	
(g)	6.85	2.74	1.00	0.00	1.00	0.00	SI	2.87	4.73	1.00		0.00	
AD1									7.19		8.69		18.96
AD2									55.89		41.97		393.2
AD3									11.62		16.95		56.40

For each line, an individual deviation called %D3 is evaluated between experimental data and model implemented with reference properties from (3)

ADi is an average deviation referring to models i=1..3 in which reference properties are from
 (1) Dharmawardhana et al. (1980) - (2) John et al. (1985) – (3) Handa and Tse (1986)
(g) experimental data from Kang et al (2000)

Table 13   Experimental data from Seo et al. (2000) and comparison to models for CO_2-CH_4 gas hydrate

	Experiment						Structure	Simulation					
			Gas Molar fraction		Hydrate Molar fraction			Pressure		Hydrate			
	T	P_{eq}						P_{eq}		Molar fraction			
	°C	MPa	CO_2	CH_4	CO_2	CH_4		MPa	%D3	CO_2	%D3	CH_4	%D3
(h)	-0,05	2,00	0,28	0,72	0,92	0,08	SI	1,87	6,59	0,46	49,93	0,54	537,5
(h)	0,95	2,00	0,40	0,60	0,94	0,06	SI	1,90	4,81	0,58	38,40	0,42	561,6
(h)	2,25	2,00	0,61	0,39	0,98	0,02	SI	1,93	3,33	0,74	24,58	0,26	1340
(h)	3,15	2,00	0,79	0,21	1,00	0,00	SI	1,96	2,24	0,87	13,01	0,13	4324
(h)	0,65	2,60	0,13	0,87	0,66	0,34	SI	2,34	9,88	0,25	62,44	0,75	122,3
(h)	1,75	2,60	0,23	0,77	0,85	0,15	SI	2,37	8,66	0,39	53,57	0,61	296,6
(h)	3,15	2,60	0,42	0,59	0,93	0,07	SI	2,40	7,52	0,58	37,40	0,42	475.0
(h)	4,35	2,60	0,64	0,36	0,98	0,02	SI	2,42	7,06	0,76	22,69	0,24	1171
(h)	4,95	2,60	0,83	0,17	0,99	0,01	SI	2,38	8,36	0,89	10,45	0,11	1731
(h)	3,45	3,50	0,13	0,87	0,65	0,35	SI	3,13	10,44	0,25	61,63	0,75	113.0
(h)	4,45	3,50	0,25	0,75	0,73	0,27	SI	3,14	10,32	0,41	44,60	0,59	122,4
(h)	5,85	3,50	0,42	0,58	0,89	0,11	SI	3,26	6,82	0,57	35,59	0,43	287,9
(h)	6,75	3,50	0,61	0,39	0,95	0,05	SI	3,26	6,82	0,73	23,62	0,27	468,4
(h)	7,35	3,50	0,83	0,17	0,99	0,01	SI	3,22	7,95	0,88	10,97	0,12	1556
AD1									10.11		36.20		770.4
AD2									9.62		35.13		976.7
AD3									7.19		34.92		936.4

For each line, an individual deviation called %D3 is evaluated between experimental data and model implemented with reference properties from (3)
ADi is an average deviation referring to models i=1..3 in which reference properties are from
 (1) Dharmawardhana et al. (1980) - (2) John et al (1985) – (3) Handa and Tse (1986)
(h) experimental data from Seo et al. (2000)

6   Conclusion

In this work, a method has been presented to evaluate the envelope curves of the three phase equilibrium between a solid hydrate, a liquid aqueous and a gaseous phase formed by ternary systems of the type {water + carbon dioxide + (nitrogen or methane)}. In the experimental part of the study measurements were carried out to generate data on the hydrate equilibria established from CO_2-N_2 and CO_2-CH_4 gas mixtures. Subsequently, the data have been described by means of the van der Waals and Platteeuw model (1959) in which the Kihara parameters had been re-calculated for an optimised set of macroscopic parameters taken from Handa and Tse (1986). Our experimental results are well correlated, both with regard to the estimation of the equilibrium pressure as well as the hydrate composition. Using this

optimised set of parameters, the model has been validated against experimental results found in the literature. At first the model had been tested against data of the system $\{H_2O + N_2 + CH_4\}$, a mixture not being investigated experimentally in this work. It turned out that the model continues to work efficiently, with regard to the estimation of both, the pressure as well as the hydrate composition. Finally, the performance of the model was tested against measured data from the literature for the systems composed of the same gas mixtures we have tested, i.e. CO_2-N_2 and CO_2-CH_4. Depending on the source of the data (Seo et al. (2000) or Kang et al. (2001)), our modelled results deviate slightly or strongly from the literature results. Whereas the equilibrium pressure is estimated correctly by our model (with a standard deviation ranging from 7 to 13%), the hydrate composition is never estimated well. This observation shows that our experimental data differ slightly or strongly from the data of these authors, too. The main difference concerns the experimental evaluation of the hydrate composition.

Acknowledgements

Annex 1 : Evaluation of error

**a) Evaluation of the initial quantity of gases in the reactor from pressure balance.**
The principle of the preparation of the gases is to generate a binary mixture (for example CO_2 and N_2) with a given molar composition ($z(A)$ and $z(B)$) by the following procedure:
0- temperature is controlled to T value
1- After vacuuming, a volume V of reactor (temperature T), inject the first gas (A) into the reactor up to a pressure P_1
2- Inject second gas (B) to a pressure P_2
3- Back calculate the molar composition n_A, n_{A+B} and $n_B = n_{A+B} - n_A$ by using the following algorithm
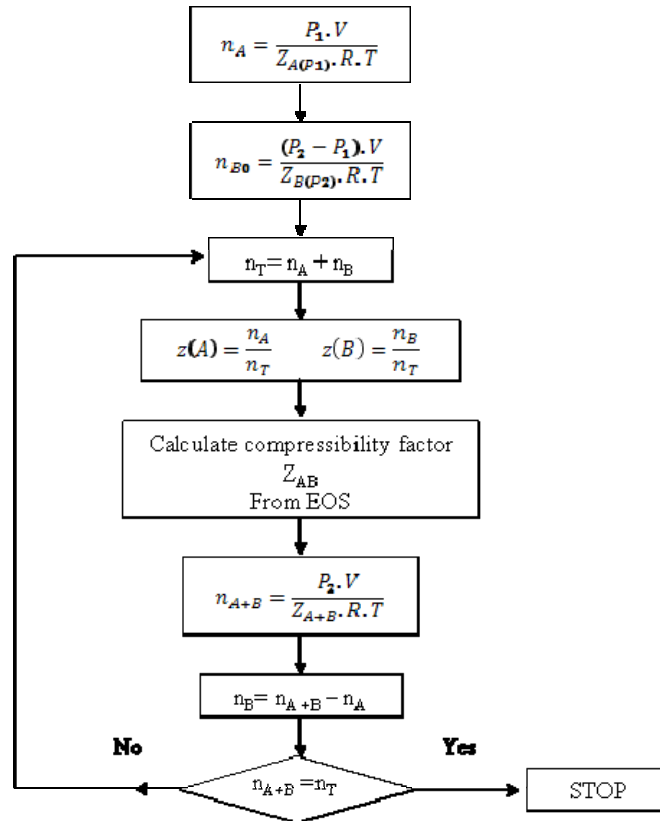
Calculation of error
After convergence, the gas composition is calculated from

$$n_A = \frac{P_1 V}{Z_{A(P1)} RT} \quad ; \quad n_{A+B} = n^G = \frac{P_2 V}{Z_{A+B(P2)} RT} \quad \text{and} \quad n_B = \frac{P_2 V}{Z_{A+B(P2)} RT} - n_A$$

So, a direct evaluation of error on n_A and n_{A+B} gives

$$\frac{\Delta n_A}{n_A} = \frac{\Delta P_1}{P_1} + \frac{\Delta V}{V} + \frac{\Delta Z_{A(P1)}}{Z_{A(P1)}} + \frac{\Delta T}{T} \quad \text{and} \quad \frac{\Delta n_{A+B}}{n_{A+B}} = \frac{\Delta P_2}{P_2} + \frac{\Delta V}{V} + \frac{\Delta Z_{A+B(P2)}}{Z_{A+B(P1)}} + \frac{\Delta T}{T}$$

So finally $\dfrac{\Delta n_B}{n_B} = \dfrac{1}{z(B)} \dfrac{\Delta n_{A+B}}{n_{A+B}} + \dfrac{z(A)}{z(B)} \dfrac{\Delta n_A}{n_A}$

- the error on evaluation of pressure is $\Delta P = 0.05 \, \text{MPa}$
- the error on evaluation of reactor is volume $\Delta V = 30 \text{ cm}^3$
- the error on the valuation of compressibility factor is not evaluated here, and considered as negligible compared to other
- the error on temperature is $\Delta T = 0.1 \text{ K}$

In regard to the precision of the instrument, the error is mainly due to the precision in the evaluation of the pressure :

$\dfrac{\Delta n_A}{n_A} \approx \dfrac{\Delta P_1}{P_1}$ and $\qquad \dfrac{\Delta n_{A+B}}{n_{A+B}} \approx \dfrac{\Delta P_2}{P_2}$ and $\qquad \dfrac{\Delta n_B}{n_B} \approx \dfrac{1}{z(B)} \dfrac{\Delta P_{A+B}}{P_{A+B}} + \dfrac{z(A)}{z(B)} \dfrac{\Delta P_A}{P_A}$

b) Calibration of the gas chromatograph

The principle of the preparation of the gases is to generate a binary mixture (for example CO_2 and N_2) with a given molar composition ($z(A)$ and $z(B)$), and to compare the ratio (S_A/S_B) of the surface of the respective chromatograph peak.

Once the gas composition is determined, a gas chromatography is performed, and the respective surface areas ratio of gas A and B ($\dfrac{S(A)}{S(B)}$) is measured and correlated to ratio of respective gas composition $\dfrac{z(A)}{z(B)}$. The peak surface area is estimated with an error $\Delta S / S$ = 0.05.
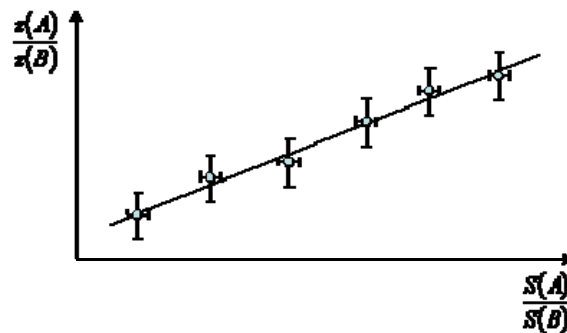
The result is a calibration curve which gives estimation of $\dfrac{z(A)}{z(B)}$ plus or minus 1%.

c) Evaluation of the error on $z(A)$ and $z(B)$ from gas chromatography

After sampling of the gas phase, once $\dfrac{S(A)}{S(B)}$ has been determined by gas chromatography, the value of $\dfrac{z(A)}{z(B)}$ is determined from the previous calibration curve :

$$a = \frac{z(A)}{z(B)} \text{ and } z(A) + z(B) = 1 \text{ ; so } z(A)\left(1 + \frac{1}{a}\right) = z(A)\frac{1+a}{a} \text{ and } z(A) = \frac{a}{1+a}$$

So, the error on the evaluation of $z(A)$ (or $z(B)$) is $\dfrac{\Delta z(A)}{z(A)} = \dfrac{\Delta z(B)}{z(B)} = \dfrac{2\Delta a}{a}$ and value of 2%

d) Evaluation of the error err_j^G of the mole number of gas in the gas phase at time t.

At time t, the composition of the gas is given form gas chromatography ($\Delta z/z = 0.02$) and pressure measurement ($\Delta P = 0.05$MPa).

$$n^G = \frac{P\,V_R}{Z(T,p,z_j)RT} \text{ and } n_j^G = n^G\, z_j$$

$$\frac{\Delta n_j^G}{n_j^G} = \frac{\Delta n^G}{n^G} + \frac{\Delta z_j}{z_j} \text{ and } \frac{\Delta n^G}{n^G} \approx \frac{\Delta P}{P} \text{ (see annex 1.a)}$$

With $\Delta P = 0.05$MPa and $=0.02$, we obtain an estimation of the error that is always superior to 2%, inferior to 3% as soon as the pressure is superior to 0.5 MPa , and inferior to 2.5% as soon as the pressure is superior to 1 MPa. In our experiments, pressure is always superior to 1 MPa, and we will retain that

$$err_j^G = \frac{\Delta n_j^G}{n_j^G} = 0.025$$

e) Evaluation of the error on the calculation of the gas mole number consumption between two steps at phase at time t1 and t2

We evaluate the error on the calculation of $n_{j0}^G - n_j^G$ that is the quantity of gas that has been transferred to solution, i.e. dissolution and crystallisation.

$$n_{j0}^G - n_j^G = \frac{P_0 V_R}{Z(T,P_0,z_{j0})RT}z_{j0} - \frac{P\,V_R}{Z(T,P,z_j)RT}z_j$$

In a good approximation, we can write

$$n_{j0}^G - n_j^G \approx \frac{V_R}{\overline{Z}RT}\left(P_0 z_{j0} - P\,z_j\right) \text{with } Z = \frac{Z(T,P_0,z_{j0}) + Z(T,P,z_j)}{2}$$

Secondly, in consideration that the evaluation of the mole number is first order depend on the precision of pressure P and composition z, we can write

$$d\left(n_{j0}^G - n\right)_j^G = \frac{V_R}{\overline{Z}RT}\left(dP_0 z_{j0} + P_0 dz_{j0} - dP\,z_j - P\,dz_j\right)$$

So

$$\Delta\left(n_{j0}^G - n_j^G\right) = \frac{V_R}{\overline{Z}RT}\left(\Delta P_0\left(z_{j0} + z_j\right) + \left(P_0 + P\right)\left(\Delta z\right)\right)$$

$$\frac{\Delta\left(n_{j0}^G - n_j^G\right)}{n_{j0}^G - n_j^G} < \left(2\frac{\Delta P_0}{P_0} + 2\left(\Delta z\right)\right) < 5\%$$

The same calculation can be done for the total amount of gas

$$\frac{\Delta\left(n_0^G - n^G\right)}{n_0^G - n^G} = 2\frac{\Delta P_0}{P_0}$$

f) Evaluation of the error err_j^L of the mole number of gas in the liquid phase at time t

Gas composition of the liquid phase is determined from an Henry correlation (see part 3.3.4, equations 7,8 and 9).

$$n_j^L = \frac{V^L \rho_w^\circ}{M_w} \frac{y_j \varphi_j^G P}{K_{H,j}^\infty \exp\left(Pv_j^\infty / RT\right)}$$

In a first approximation, we can write that

$$\frac{\Delta n_j^L}{n_j^L} = \frac{\Delta V^L}{V^L} + \frac{\Delta K_{H,j}^\infty}{K_{H,j}^\infty} + \frac{\Delta P}{P}$$

with $V^L = \frac{V_0^L [Li^+]_0}{[Li^+]}$ and so $\frac{\Delta V^L}{V^L} = \frac{\Delta V_0^L}{V_0^L} + \frac{\Delta[Li^+]_0}{[Li^+]_0} + \frac{\Delta[Li^+]}{[Li^+]}$

$\frac{\Delta V_0^L}{V_0^L} << 0.001$ because it is determined from mass measurement, with precision of 0.01g and

total mass of water around 1 kg.

$\frac{\Delta[Li^+]}{[Li^+]} << 0.001$ in reason of the precision of the ionic chromatography

So, we can give an evaluation of

$$\frac{\Delta n_j^L}{n_j^L} \approx \frac{\Delta K_{H,j}^\infty}{K_{H,j}^\infty} + \frac{\Delta P}{P}$$

Without an evaluation of the precision of the Henry constant, we will overestimate it to 10%,

so that $err_j^L = \frac{\Delta n_j^L}{n_j^L} \approx 0.1$. We will see after there is no consequence on the evaluation of the

mole number of gas in the hydrate phase (see following) because of low quantity of gas in the liquid phase in respect to the quantity in the gas phase and hydrate phase;

g) Evaluation of error of the mole number of gas in the hydrate phase.
The mole number of gas in the hydrate phase is calculated from a mass balance from equation (1)

$$n_j^H = n_j^L + n_j^G - n_{j,0}$$

In a first approximation, because of the very low solubility of gases in water, we have also

$$n_j^L << n_j^H \text{ and } n_j^H \approx n_j^G - n_{j,0}$$

So

$$\frac{\Delta n_j^{\mathrm{H}}}{n_j^{\mathrm{H}}} \approx \frac{\Delta\left(n_j^{\mathrm{G}} - n_{j,0}\right)}{n_j^{\mathrm{G}} - n_{j,0}} = 5\% \text{ from annex 1.e}$$

h) Evaluation of the error on the calculation of composition (molar fraction) of gas in the hydrate

In a first approximation that assumes the quantity of gas in liquid is negligible compared to other quantities (hydrate and gas phases), we can write :

$$x_j^H = \frac{n_j^{\mathrm{H}}}{\sum_i n_i^{\mathrm{H}}} = \frac{n_j^{\mathrm{H}}}{n_0^{\mathrm{G}} - n^{\mathrm{G}}}$$

$$dx_j^H = \frac{dn_j^{\mathrm{H}}}{n_0^{\mathrm{G}} - n^{\mathrm{G}}} - \frac{1}{\left(n_0^{\mathrm{G}} - n^{\mathrm{G}}\right)^2} n_j^{\mathrm{H}} d\left(n_0^{\mathrm{G}} - n^{\mathrm{G}}\right) \text{ that gives}$$

$$\Delta x_j^H = \frac{\Delta n_j^{\mathrm{H}}}{n_0^{\mathrm{G}} - n^{\mathrm{G}}} + \frac{n_j^{\mathrm{H}}}{n_0^{\mathrm{G}} - n^{\mathrm{G}}} \frac{\Delta\left(n_0^{\mathrm{G}} - n^{\mathrm{G}}\right)}{n_0^{\mathrm{G}} - n^{\mathrm{G}}}$$

With (annex 1.e) $\dfrac{\Delta\left(n_0^{\mathrm{G}} - n^{\mathrm{G}}\right)}{n_0^{\mathrm{G}} - n^{\mathrm{G}}} = 2\dfrac{\Delta P_0}{P_0}$ we get $\Delta x_j^H = \dfrac{n_j^{H}}{n^{H}} 0.05 + \dfrac{n_j^{H}}{n^{H}} 0.01$

So, finally, the evaluation is

$$\frac{\Delta x_j^H}{x_j^H} < 0.06$$

Nomenclature/List of symbols

<u>Latin letters:</u>

A	Coefficient in correlating equation for Henry's law constant, and in Parrish and Prausnitz' equation, respectively
a	Activity [-] or Kihara parameter, spherical nucleus radius [m]
B	Coefficient in correlating equation for Henry's law constant [K^{-1}], and in the Parrish and Prausnitz relation, respectively
b	Coefficient lineary temperature dependency of the heat capacity [$J\ mol^{-1}\ K^{-2}$]
C	Langmuir constant of cavity
c	Molar heat capactiy [$J\ mol^{-1}\ K^{-1}$]
F	Objective function in the difference of the chemical potential differences
f	Fugacity [Pa]
h	Molar enthalphy [$J\ mol^{-1}$]
K_H	Henry's constant at saturation pressure of the pure solvent, i.e., at infinite dilution of the gaseous component [Pa^{-1}]
k	Boltzmann constant [$J\ K^{-1}$]
N	Number of points of a given set of data
n	Mole number
P	Pressure [Pa]
R	Gas molecule equivalent radius [m] or universal gas constant [8.314472 $m^2\ kg\ s^{-2}\ K^{-1}\ mol^{-1}$]
r	Distance between the molecule and the wall of the cavity [m]
T	Temperature [K]
V	Volume [m^3]
v	(Partial) molar volume [$m^3\ mol^{-1}$]
w	Potential energy function
x	Mole fraction in the liquid or solid phase
y	Mole fraction in the gas phase
Z	Compressibility factor
z	Coordination number of the cavity in which a molecules is enclatrated [-]

<u>Greek letters:</u>

γ	Activity coefficient [-]

Δ	Difference operator
ε	Kihara parameter, maximum attraction potential [-]
μ	Chemical potential [J mol^{-1}]
ν	Number of cavities per molecules of water [-]
θ	Occupation rate of cavity/gas
ρ	(Mass) Density of water [kg m^{-3}]
σ	Kihara parameter, distance between the molecules and the cavity wall, at null potential [m]

Subscripts:

i	Index characterising the type of cavities ($i = 5^{12}$, $5^{12}6^2$ or $5^{12}6^4$)
j, k	Index representing component
l	Index representing experimental data point l
p	Isobaric property
R	Index referring to reactor
w	Water
0	Referring to initial condition

Superscripts:

I	Ice phase
H	Hydrate phase
L	Liquid phase
G	Gas/Vapour phase
β	Hypothetical reference phase for the hydrate phase corresponding to empty lattice
$\varphi - \beta$	Referring to the difference between any phase and the reference phase b
∞	Corresponding to the state of infinite dilution
0	Corresponding to reference values for T and/or P
$\circ$	Corresponding to pure component property

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