# Gas hydrate equilibria for CO2-N2 and CO2-CH2 gas mixtures, experiments and modelling

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# GAS HYDRATE EQUILIBRIA FOR $CO_2$-$N_2$ AND $CO_2$-$CH_4$ GAS MIXTURES, EXPERIMENTS AND MODELLING

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## ABSTRACT

$CO_2$ capture in industry is regarded as a possible tool that is suitable for reducing the global carbon emissions. The gases emitted by industry are by definition localized at the plants, like steelmaking plants, gas or coal power plants, chemical plants or natural gas production plants.
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 used as an alternative approach to remove green house gases, and this is the route we try to develop here. A preliminary costing has revealed the process to be competitive for high concentrated mixtures of $CO_2$ containing $N_2$ [1] such as found in exhaust gases of steel making plants at atmospheric pressure.
This work presents a set of experimental data on the hydrate liquid vapour equilibria encountered in the mixtures of $CO_2$-$N_2$ and $CO_2$-$CH_4$ 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 [2] 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 thermodynamic approach).
Due to large deviations between the modelled 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 [3] 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 falsified against other sources.

*Keywords*: gas hydrates, gas mixtures, thermodynamics

## INTRODUCTION

$CO_2$ capture in industry is a challenging task. It is seen as a possible tool for making a significant contributing to the reduction of 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 suitable industrial processes 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 of $CO_2$ per second. 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

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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 in this work. 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 hydrate liquid vapour equilibria in systems comprised of the binary gas mixtures $CO_2$-$N_2$ and $CO_2$-$CH_4$, respectively, and 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.

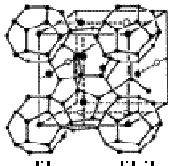
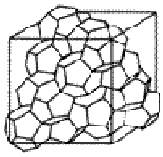
Furthermore we have tried to validate our experimental data by using the classical van der Waals and Platteeuw model (1959) with internal parameters found in the literature. These parameters are the so-called macroscopic parameters (i.e. macroscopic parameters from Table 2 which refer to a classical 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 or falsified against experimental data available in the literature.

## HYDRATES STRUCTURES

Three different hydrate structures have been identified experimentally, which are denoted by sI, sII and SH. They differ by their crystallographic structure in which water is organized in a three dimensional network which provides internal cavities of different polyhedra cavities called $5^{12}$, $5^{12}6^2$, $5^{12}6^4$, $4^35^66^3$ and $5^{12}6^8$ ($e^f$ describes a polyhedra: $e$ is the number of edges of the face, and $f$ is the number of faces with $e$ edge). In Table 1 the SI and SII are described more precisely structure that can be only formed in respect to the nature of the Martian gases.

Table 1
Structure of SI and SII gas Hydrates

| | SI | | SII | |
|---|---|---|---|---|
| |  | |  | |
| Cavity | $5^{12}$ | $5^{12}6^2$ | $5^{12}$ | $5^{12}6^4$ |
| Type of cavity (j: indexing number) | 1 | 2 | 1 | 3 |
| Number of cavities ($n_j$) | 2 | 6 | 16 | 8 |
| Average cavity radius (nm) (1) | 0.395 | 0.433 | 0.391 | 0.473 |
| Variation in radius, % (2) | 3.4 | 14.4 | 5.5 | 1.73 |
| Coordination number | 20 | 24 | 20 | 28 |
| Number of water molecules | 42 | | 136 | |
| Cell parameters (nm) | a= 1.1955 (3) | | a=1.7315 (4) | |
| Cell volume ($nm^3$) | 1.709 (3) | | 5.192 (4) | |

(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).

## EXPERIMENTAL PROCEDURE AND APPARATUS

An experimental apparatus (figure 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) equipped 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 1000 ml (or 0.8 l to 1 l) of water containing $LiNO_3$ as an anionic tracer at a concentration of approximately 10 to 15 ppm (weight fraction). 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 means of a pressure transducer (Keller instrument, range: (0-10) MPa, precision of 0.05 MPa). The (*T*, *P*) data acquisition unit 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 $\mu m^3$) which is directly injected into the loop of the gas chromatograph (VARIAN model CP-3800 GC). The precision in gas composition is 2% (see Herri et al., 2011)

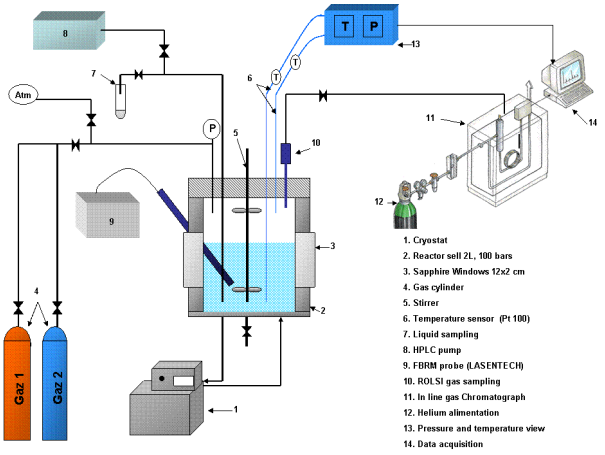



Figure 1
Experimental set up

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 mixture (see Herri et al., 2011).

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)).

*Experimental procedure*

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.

Subsequently, the stirrer is started and 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. During the formation of the solid, the pressure decreases due to the gas consumption to form hydrates. While the crystallization takes place, 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 method to evaluate the experimental results is presented in detail in Herri et al., 2011). The method outlined above results in the determination of the complete set of quantities charaterising the phase equilibrium condition. In other words, the approach enables the experimental determination of the tuple of values of temperature, pressure, and the compositions of the gas and hydrate phases, respectively .

**MODELLING**

The so-called van der Waals and Platteeuw model (van der Waals and Platteeuw, 1959) has been explained in many publications and books on the subject (see, e.g., Sloan, 1998). Our objective is not to present the details of the model equations again, but to recall the input data which we focused on in this work.

In the case of hydrates, in thermodynamic equilibrium, the equality of the chemical potentials of water in the ice, liquid as well as in the hydrate phase, respectively, can be written by introducing a reference state which is a hypothetical phase β corresponding to a hydrate with empty cavities.

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

where $\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta}$ and $\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta}$ are the differences of the chemical potentials between the water in the hydrate or liquid phase and in the reference phase, respectively.

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

$\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta}$ is then determined from statistical thermodynamics whereas $\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta}$ is determined by means of relations originating from classical thermodynamics.

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

In eq. (2) $\nu_i$ is the number of cavities of type $i$ per molecule of water 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.

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. It can be expressed as a function of the fugacity $f_j$ of the gas $j$ as:

$$\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta} = RT\sum_i \nu_i \ln\left(1-\sum_j C_j^i f_j(T,P)\right) \qquad (3)$$

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 spherical symmetrical cage that can be described by a spherical symmetrical potential:

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

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 (van der Waals and Platteeuw, 1959), the Parrish and Prausnitz model (Parrish and Prausnitz , 1972) or the so-called Kihara model. The latter, being the most precise (McKoy, 1963), can be expressed as:

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

$$\delta^N = \frac{1}{N}\left[\left(1-\frac{r}{R}-\frac{a}{R}\right)^{-N}-\left(1+\frac{r}{R}-\frac{a}{R}\right)^{-N}\right] \qquad (6)$$

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 data.

Modelling of $\Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta}$

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 in the phase under consideration (the liquid aqueous phase in our case, but it could be an ice or the

vapour phase) and the (hypothetical) empty hydrate phase $\beta$, $\Delta\mu_w^{L-\beta}$ can be written as follows:

$$\Delta\mu_w^{L-\beta} = T\frac{\Delta\mu_w^{L-\beta}\Big|_{T^0,P^0}}{T^0} - T\int_{T^0}^{T}\frac{\Delta h_w^{L-\beta}\Big|_{P^0}}{T^2}dT + \int_{P^0}^{P}\Delta v_w^{L-\beta}\Big|_T dP - RT\ln a_w^L\Big|_{T,P} \quad (7)$$

The activity of water in the ice phase is 1, and if water is present 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, $\gamma_w^L$, 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 $a_w^L \cong x_w$.

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

$$\Delta h_w^{L-\beta}\Big|_{P^0} = \Delta h_w^{L-\beta}\Big|_{T^0,P^0} + \int_{T^0}^{T}\Delta c_{p,w}^{L-\beta}\Big|_{P^0}dT \quad (8)$$

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

$$\Delta c_{p,w}^{L-\beta}\Big|_{P^0} = \Delta c_{p,w}^{L-\beta}\Big|_{T^0,P^0} + b_{p,w}^{L-\beta}\left(T - T^0\right) \quad (9)$$

Table 2
Reference state parameters

| | Unit | Structure I | Structure II |
|---|---|---|---|
| $\Delta\mu_w^{L-\beta,0}$ | J mol$^{-1}$ | 1287 | 1068 |
| $\Delta h_w^{I-\beta,0}$ | J mol$^{-1}$ | 931 | 764 |
| $\Delta v_w^{L-\beta}\Big\|_{T^0}$ | $10^{-6}$ m$^3$ mol$^{-1}$ | 4.5959 | 4.99644 |
| $\Delta c_{p,w}^{L-\beta,0}$ | J mol$^{-1}$ K$^{-1}$ | -38.12 | -38.12 |
| $b_{p,w}^{L-\beta}$ | J mol$^{-1}$ K$^{-2}$ | 0.141 | 0.141 |

$\Delta\mu_w^{L-\beta,0}$, $\Delta h_w^{I-\beta,0}$: Handa and Tse, 1986

$\Delta v_w^{L-\beta}\Big|_{T^0}$, $\Delta c_{p,w}^{L-\beta,0}$, $b_{p,w}^{L-\beta}$: Sloan, 1998

**Equilibrim**

Equilibrium is achieved when $\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta}$ is achieved.

A minimization algorithm has been implemented in the GasHyDyn Sofware (Java language) to determine the state variables, i.e., P, T, gas composition, and hydrate composition at equilibrium computationally by using kihara parameters and reference state parameters as input quatities, or inversely, to determine the set of these parameters from (P, T, gas composition, hydrate composition) experimental data (more details can be found in Herri et al., 2011)

The idea behind this work was to generate an auto-coherent set of parameters. In fact, when taking a look at the literature, we can notice the variation in the numerical values of both Kihara parameters, but also reference state parameters that have been published.

Table 3
Reference state parameters

| | Unit | Structure I | Structure II |
|---|---|---|---|
| $\Delta\mu_w^{L-\beta,0}$ | J mol$^{-1}$ | 1297(1)<br>1120 (2)<br>1287 (3) | 937 (1)<br>1714 (2)<br>1068(3) |
| $\Delta h_w^{I-\beta,0}$ | J mol$^{-1}$ | 1389 (1)<br>931(2)<br>931 (3) | 1025 (1)<br>1400 (2)<br>764 (3) |
| $\Delta v_w^{L-\beta}\Big\|_{T^0}$ | $10^{-6}$ m$^3$ mol$^{-1}$ | 4.5959 | 4.99644 |
| $\Delta c_{p,w}^{L-\beta,0}$ | J mol$^{-1}$ K$^{-1}$ | -38.12 | -38.12 |
| $b_{p,w}^{L-\beta}$ | J mol$^{-1}$ K$^{-2}$ | 0.141 | 0.141 |
| $\Delta h_w^{L-\beta,0} = \Delta h_w^{I-\beta,0} - 6011$, where 6011 is the enthalpy of fusion of Ice (J mol$^{-1}$) | | | |

(1) refers to Dharmawardhana et al. (1980)
(2) refers to John et al (1985)
(3) refers to Handa and Tse, 1986

$\Delta v_w^{L-\beta}\Big|_{T^0}$, $\Delta c_{p,w}^{L-\beta,0}$, $b_{p,w}^{L-\beta}$: Sloan, 1998

The classical way to fit the Kihara parameters is firstly to suppose a set of reference state parameters, and secondly to benefit from a rich data base implementing not only (pressure and temperature) equilibrium data but also equilibrium data for gas mixtures. In this second case, the ideal case is to benefit from the most complete set of (pressure, temperature, gas composition and hydrate composition) data.

Subsequently, in order to retrieve Kihara parameters, the work consists in supposing a

hydrate structure (sI, sII or sH) and then to fit calculated equilibrium data with experimental data.

As a result of the approach outlined above, the Kihara constants are dependent on the reference state parameters that have been selected. In the next part of the work, we will evaluate the performance of three models. Model 1 is the model implemented with the values for $\Delta\mu_{w}^{L-\beta,0}$ and $\Delta h_{w}^{L-\beta,0}$ as published by Dharmawardhana et al. (1980), model 2 is implemented with the set of values published by John et al. (1985) and model 3 is implemented with the values from Handa and Tse (1986).

**Table 4** 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 | | | |
| | $\vartheta$ | $P_{eq}$ | | | | | | $P_{eq}$ | | | | | |
| | °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 which displays the difference between the experimental result and the corresponding value calculated by the 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 5** Experimental data and comparison to models for $CO_2$- $N_2$ gas hydrates

| | Experiment | | | | | | Structure | Simulation | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Gas Molar fraction | | Hydrate Molar fraction | | | Pressure | | Hydrate Molar fraction ± 0.06 | | | |
| | $\vartheta$ | $P_{eq}$ | | | | | | $P_{eq}$ | | | | | |
| | °C | MPa | $CO_2$ | $N_2$ | $CO_2$ | $N_2$ | | MPa | %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 which displays the difference between the experimental result and the corresponding value calculated by the 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 6** Kihara parameters regressed from experimental results of this study, and Kihara parameters from literature

| | Kihara parameters regressed from experimental results of this study and implemented in model 1,2,3 with macroscopic parameters from table 3<br>(1)Dharmawardhana et al, 1980 - (2) John et al, 1985 – (3) Handa an Tse, 1986 | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | $CO_2$ | | | $CH_4$ | | | $N_2$ | | |
| | $\frac{\varepsilon}{k}$ | $\sigma$ | $a$ | $\frac{\varepsilon}{k}$ | $\sigma$ | $a$ | $\frac{\varepsilon}{k}$ | $\sigma$ | $a$ |
| 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 |

Table 4 and Table 5 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. Table 4 and Table 5 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 4 shows the comparison of the modelling results with experimental data 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 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 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%).

**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 7. 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.

**Table 7** 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 | | | |
| | $\vartheta$ | $P_{eq}$ | | | | | | $P_{eq}$ | | | | | |
| | °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 which displays the difference between the experimental result and the corresponding value calculated by the 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)

**Conclusion**

We proposed a new set of Kihara parameters for the components $CO_2$, $CH_4$ and $N_2$ (Table 6). They are associated with the classical van der Waals and Platteeuw model (1959) implemented with reference state parameters from Handa and Tse (1986) and completed with additional parameters from Sloan (1998) (Table 6). This set of parameters allows us to predict correctly the complex HLV phase equilibrium data (pressure, temperature, gas composition, hydrate composition). The calculated data are presented in this paper along with the original experimental results on the hydrate systems formed by the binary gas mixtures $CO_2$-$CH_4$ and $CO_2$-$N_2$. Finally, the set of parameters is compared to literature data concerning the $N_2$-$CH_4$ –mixture and reveals to correct.

**Perpective**

Our set of parameters needs to be confronted with other experimental data. This work has been presented in Herri et al. (2011). It reveals for the systems generated from the $CO_2$-$N_2$ and the $CO_2$-$CH_4$ mixtures, respectively, that our experimental data differ from the data of Seo et al. (2000) and Kang et al. (2001), but in turn, that the data of Seo et al. (2000) also differs from the data of Kang et al. (2001). The results of this study raise the question of the validity of our experimental results, but also of the data of Seo et al. (2000) and Kang et al. (2001). However, they may also raise the question of a possibly different stability diagram of such mixed gas hydrates.

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