Carbon dioxide, argon, nitrogen and methane clathrate hydrates: Thermodynamic modelling, investigation of their stability in Martian atmospheric conditions and variability of methane trapping

Jean-Michel Herri, Eric Chassefière

1   **Carbon dioxide, argon, nitrogen and methane clathrate hydrates:**

2   **thermodynamic modelling, investigation of their stability in Martian**

3   **atmospheric conditions and variability of methane trapping**

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1

1   **Abstract**

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3   This paper deals with the stability of clahtrate hydrates at low temperature and low pressure in the

4   conditions prevailing in the atmosphere and at the surface of Mars. We fit the classical van der

5   Waals model to compare deviation from experimental results published in the literature. It appears

6   to be acceptable and allows to simulating a Martian gas, CO_2 dominated (95.3%) plus nitrogen

7   (2.7%) and argon (2%). The hydrate is a CO_2-based hydrate which is unstable during Mars'

8   summer and stable during Mars' winter. The proportion of methane in the hydrate is estimated and

9   is found to be from one tenth to one third of the composition of the gas phase. The proportion

10   depends on the crystallographic structure which is assumed to be formed. In fact, both the structure

11   I and II appear to be stable in the conditions of Mars' winter. The consequences of these results on

12   our understanding of the atmospheric cycle of Martian methane are drawn and analyzed. We

13   propose upper limits on (i) the seasonal variation of methane due to a hypothesized alternate

14   formation of $CO_2/N_2/Ar/CH_4$ hydrates on the seasonal polar caps, and (ii) on the lifetime of

15   atmospheric methane with respect to an hypothesized continuous trapping under hydrate form on

16   the south polar cap. We show that these mechanisms have only small effects, and cannot play a

17   significant role in the dynamics of methane in present Mars'atmosphere. Hypothesized clathrate

18   hydrates trapped in the permanent south polar cap could include methane in relative proportions

19   between 0.1 and 0.4 times the average global atmospheric ratio. Searching for the spectral

20   signatures of clathrate hydrates on the caps and, if detectable, of inhomogeneities of the CH_4

21   mixing ratio in possible local atmospheric plumes forming during the sublimation of polar hydrate

22   pockets in spectroscopic data from existing (Mars Express, MRO) and future (TGO-Exomars)

23   missions is an interesting challenge of Mars science and astrobiology.

24

1   *Keywords*: Mars, clathrate hydrate, nitrogen, carbon dioxide, argon, methane, equilibrium

Introduction

Methane has been detected in Mars' atmosphere from both Earth and orbital probes (Mars Express, Mars Global Surveyor) at an average ~10-20 ppb level (Krasnopolsky et al., 2004; Formisano et al., 2004; Mumma et al., 2009; Fonti and Marzo, 2010; Geminale et al., 2011). One of the most striking characteristics of the observed CH_4 is its high temporal and spatial variability, implying a lifetime of 200 days (Lefèvre and Forget, 2009), much shorter than the currently admitted value of 300 yr based on existing photochemical models (see e. g. Krasnopolsky, 2006). The nature of CH_4 sink is unknown. Spacecraft data (MGS, Mars-Express) which now span ~6 Martian years (MY24-MY29) and Earth-based measurements show a globally consistent and reproducible seasonal behavior of the CH_4 mixing ratio, with definitely less CH_4 in the atmosphere during northern winter. More generally, existing observations show that CH_4 is spatially and temporally highly variable (Fonti and Marzo, 2010; Geminale et al., 2011). The origin or methane is not known. It could have been produced by hydrothermal processes in the crust (Oze and Sharma, 2005; Lyons et al., 2005), or possibly biogenically (Atreya et al., 2006), then stored in the cryosphere under the form of hydrates for long periods of time before being released to the atmosphere (Chassefière and Leblanc, 2011, Chastain and Chevrier, 2007). The space and time variability of atmospheric CH_4 is still poorly understood. One possible explanation could be the erosion within the atmosphere of suspended metastable CH_4 clathrate hydrate particles by condensation/sublimation processes (Chassefière, 2009). Adsorption in the regolith, although significant, has been shown to play a minor role in the CH_4 seasonal variability (Meslin et al., 2011). Also none of the mechanisms presented has kinetics fast enough to explain the very rapid variations of methane in the atmosphere.

The goal of the present paper is to investigate the possible contribution of an hypothesized alternate $CO_2/N_2/Ar/CH_4$ clathrate hydrate formation cycle, resulting from the alternate condensation of CO_2 and H_2O on seasonal hemispheric polar caps, on the seasonal cycle of CH_4. A model of the (Pressure-Temperature) equilibrium of clathrate hydrates in the atmosphere of Mars is presented. Following the contributions of Chastain and Chevrier (2007) and Thomas et al. (2009), we applied a model based on the approach of van der Waals and Platteeuw (1959). Chastain and Chevrier (2007) and Thomas et al. (2009) have simulated the equilibrium conditions of hydrate stability in Martian conditions by extrapolating the model to very low temperature. Our contribution is to validate this extrapolation by comparing the model to experimental data at low temperature. We point the necessity to modify the internal parameters, and especially the Kihara parameters. Our contribution strengthens the conclusion of Chastain and Chevrier (2007) about the stability of gas hydrate on Mars. We conclude also that gases are fractionated from atmosphere to hydrate with fractionation factors similar to the ones proposed by Thomas et al. (2009).

For pure gases and in winter Martian conditions (temperature estimated in the range from 140-160 K), the model reveals to fit experimental data in the range 140-273 K with a mean deviation of 4-20%, depending on the gas. Then, modelling is applied to a gas which composition is that of the atmosphere of Mars. The hydrate appears to be a CO_2-based hydrate which is stable at temperature below 150 K (Structure II being assumed to form) or 148.8 K (Stucture I being assumed to form). We have used a pressure at the surface of Mars of 0.6 kPa. The pressure of Mars' atmosphere seasonally varies in the range from 0.6 to 0.9 kPa. By using a slightly different value of 0.9 kPa (Thomas et al, 2009), the hydrate is stable at temperature below 154 K (Structure I) or 156.8 K (Structure II). It results that the Martian gas hydrate is strongly suspected to be stable during the winter season. The proportion of methane in the hydrate is estimated and compared to the

estimation performed by Thomas et al. (2009). The consequences of the results on the seasonal and long-term variability of atmospheric CH_4 are presented and discussed.

Modelling

Introduction

The van der Waals and Platteeuw (1959) model describes the equilibrium of hydrate phases by means of a convergence between a statistical thermodynamics approach implementing Kihara parameters and a classical approach implementing reference state parameters. It is the most common model used because of its physical relevance and easy implementation in codes. In a recent publication (Herri et al, 2011), we have optimized the Kihara parameters versus the different sets of reference state parameters which are published in the literature (Dharmawardhana et al., 1980; John et al., 1985; Handa and Tse, 1986). The Kihara parameters have been optimized to fit equilibrium data concerning methane, carbon dioxide and nitrogen, taken as pure gases or in mixtures. Equilibrium data were not only classical (Pressure,Temperature) equilibrium curves but also the envelope curves for gases mixtures consisting in (Pressure, Temperature, gas composition, hydrate composition) equilibrium data. We observed the Handa and Tse (1986) reference state parameters to be the best to fit our data. In the following work, we use these reference state parameters to simulate hydrate equilibrium in Mars condition. In Herri et al (2011), the Kihara parameters have been optimized in (Pressure, Temperature) conditions for which we can get a maximum of experimental data from literature, obtained mainly at Earth's ambient temperature 273-293 K and pressures in the range from 1 to some tens MPa. The ambient Martian conditions are very different. Pressure varies over Mars surface from 0.3 to 1 kPa depending on location and

season. In winter period, on the southern permanent CO_2 ice polar cap, the temperature can be as low as 148 K (temperature of CO_2 condensation at 0.6 kPa) and even reach 143 K due to the high altitude of the top of the south polar cap. During the summer period, at low latitude and sunny time, temperature can reach 273 K exceptionally.

So, the possibility to extrapolate the van der Waals and Platteeuw models from Earth's conditions to Martian conditions needs to be carefully examined. In this paper, we validate the model against available data of pure gas hydrates in Martian conditions. We observe that the Kihara parameters need to be optimized again and are different from the ones optimized at positive temperature (Herri et al, 2011).

The composition of the Martian atmosphere is CO_2 dominated (95.3%) plus nitrogen (2.7%) and Argon (2%) and traces of other compounds: O_2 (1200±100 ppm), CO (700±200 ppm), H_2O (<1000 ppm with an average at 200 ppm), H_2 (20 ppm), O_3 (<0.2 ppm) and CH_4 (<50ppb with an average at 15 ppb) (Owen et al., 1977; Mumma et al., 2009) .

Hydrate structure

Three different structures have been identified : SI, SII and SH. They differ by their crystallographic structure in which water is organized in a three dimensional network. It liberates internal cavities of different polyhedral 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 polyhedron: e is the number of edges of the face, and f is the number of faces with e edge). In Table 1 are described more precisely the SI and SII structures, the only ones that can be formed due to the nature of the Martian gases.

<div align="center">

Table 1

</div>

Modelling

In the case of hydrates, in thermodynamic equilibrium, the equality of chemical potentials of water in the ice (or liquid) phase and in the hydrate phase can be written by introducing a reference state which is a hypothetical phase β that corresponds to a hydrate with empty cavities.

$$\Delta\mu_{\text{w}}^{\text{H}-\beta} = \Delta\mu_{\text{w}}^{\text{L}-\beta} \tag{1}$$

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.

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

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

$$\Delta\mu_{\text{w}}^{\text{H}-\beta} = RT \sum_{i} v_i \ \ln\left(1 - \sum_{j} \theta_j^i\right) \tag{2}$$

In Eq. (2) v_i is the number of cavities of type i per mole of water 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 essential 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:

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

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

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

(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 (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:

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

(5)

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

(6)

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 is only dependent on the properties of the gases (via the Kihara parameters), and on the geometrical properties of the cavities (through their coordination number z and their average mean radius $\bar{R}$, see Table 2).

Table 2

Modelling of $\Delta \mu_w^{\varphi - \beta}$

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 between the reference phase (Ice in our case, but it could be liquid phase or vapour phase) and the (hypothetical) empty hydrate phase β, $\Delta \mu_w^{\varphi - \beta}$, can be written as follows:

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

The activity of water in the ice is 1. If liquid water is present, 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 $a_w^L \cong x_w$.

A refinement of the model is given by Sloan (1998, 2008) that takes into account the temperature dependence of the difference of molar enthalpy $\left.\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\right|_{P^0}$ (J/mol H_2O) using the well-known classical thermodynamic relationship

$$\left.\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\right|_{P^0} = \left.\Delta h_{\mathrm{w}}^{\mathrm{L}-\beta}\right|_{T^0,\,P^0} + \int_{T^0}^{T} \left.\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\right|_{P^0} dT \tag{8}$$

assuming a linear dependence of the difference of molar heat capacity $\left.\Delta c_{p,\,\mathrm{w}}^{\mathrm{L}-\beta}\right|_{P^0}$ (J/K/mol H_2O) on temperature according to :

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

The values of the reference state parameters are given in Table 3.

Table 3

Equilibrium

Equilibrium is achieved as equality of $\Delta\mu_{\mathrm{w}}^{\mathrm{H}-\beta} = \Delta\mu_{\mathrm{w}}^{\mathrm{L}-\beta}$ is achieved.

A minimization algorithm has been implemented in GasHyDyn Sofware (Java language), to determine (P, T, gas composition, hydrate composition) equilibrium from computing by using Kihara parameters and reference state parameters, or inversely, to determine parameters from (Pressure, Temperature, gas composition, hydrate composition) experimental data base (more details may be found in Herri et al, 2011).

The procedure is the following. First, according to Mehta and Sloan (1996), the value of *a* is fixed by using the correlation of Tee et al (1996). Then, 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 to the value such as $\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta}$. 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:

$$F(\varepsilon_j, \sigma_j) = \sum_{l=1}^{N} \left| \frac{P_{calc}}{P_{exp}} - 1 \right| \rightarrow \min \text{ (resp. } F(\varepsilon_j, \sigma_j) = \sum_{l=1}^{N} \left| \frac{T_{calc}}{T_{exp}} - 1 \right| \rightarrow \min \text{)} \qquad (10)$$

In Eq. (10), the index *l* assigns the specific data point and the summation has to be performed over all *N* data of the set.

Kihara parameters given in Table 2 are optimized to minimize the error and fit the experimental results at low temperature implemented in the data base which is detailed below.

Data Base

The data base of GasHyDyn Sofware has been completed with the data at low temperature compiled in the review of Fray et al. (2010) concerning methane and CO_2 clathrate below the ice points. Very few data can be found for N_2 clathrate below the point, and in a very limited range of temperature of 261.7-270K (Mohammadi and Richon, 2010). For argon, few data has been found but in a wide range of temperature of 90 to 291 K in Holder et al., 1980 (original data from Saito and Kobayashi, 1965, and original data from Barrer and Edge, 1967). Data have been completed with the first two points of the history from de Forcrand (1923).

Comment on the geometric description of the cavity

Theoretically, in equation 4, the interaction potential $w(r)$ needs to be 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 inside which the gas molecule is encapsulated), but also interacts with other molecules localized away from it. In fact, John and Holder (1982) have showed that 2nd and 3rd hydration shells contribute significantly to the Langmuir constant with a resulting change of this Langmuir constant by 1-2 orders of magnitudes (Sparks and Tester, J.W., 1992). Also, even with a rigorous integration of the interaction potential over all the hydration shells, the John and Holder model (1982) can give rigorous results only for spherical molecules (such has Kr, Ar, CH_4…). John et al (1985) have introduced a correction factor to take into account the asymmetry of the encapsulated molecules. All these refinement methods tend to give a physical signification to the interaction potential $w(r)$ 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.

Comment on the reference properties

Special attention has to be paid when assigning value for $\Delta\mu_w^{L-\beta}\big|_{T^0,P^0}$ in Eq. (8) and $\Delta h_w^{L-\beta}\big|_{T^0,P^0}$ in Eq. (7) since the corresponding data found in the literature vary strongly from one author to the other, mainly due to the difficulties arising when determining these quantities experimentally. The values can be found in the open literature as cited by Sloan (1998, 2007). However, in a previous work (Herri et al, 2010), we tested the different values in simulating the equilibrium conditions and composition of phases for gas hydrates formed from gas mixtures (CO_2-N_2), (CO_2-CH_4) and (CH_4-N_2) and liquid water. We observed the values of Handa and Tse (1986) to be the best ones.

Conclusion of comments

In the end, the Kihara parameters remain adjustable parameters. As it has been claimed by John et al (1987) and reported by Mehta and Sloan (1996): the wrong kihara parameters, wrong cell potential, wrong Langmuir constants (and we can add from Herri et al (2010) the wrong reference parameters) could still lead to the right dissociation pressures.

Simulation of Martian Hydrates

The equilibrium is at first order governed by the dominating gas (CO_2, 95.7%) and secondly affected by second order constituents (N_2, 2.7%, and Ar, 2%). It is not affected by very low concentration components such as O_2 (1200±100 ppm), CO (700±200 ppm), H_2O (<1000 ppm, with an average of 200 ppm), H_2 (20 ppm), O_3 (<0.2 ppm) and CH_4 (<50 ppb with an average of 15 ppb). Methane gas is a trace, but we will model it as precisely as possible because we want to understand its repartition between atmosphere and solid hydrate.

Pure gas equilibrium in atmospheric Martian conditions

Pure CO_2 hydrates

Figure 1 plots the deviation between the experimental data and simulation depending on the values of ε and σ. We compare 32 experimental results from Yasuda and Ohmura (2008), Adisasmito et al. (1991), Falabella (1975), Miller and Smythe (1970) which cover a range of temperature from 151.52K to 282.9K and a pressure range from 0.535kPa to 4370kPa. In Figure 1, we can see that

the ε and σ values which minimize the deviation are located in a deep valley. The figure 2 plots the ε and σ values in the valley, and the corresponding deviation. The minimum deviation corresponds to values of ε and σ reported in Table 2.

Figure 1

Figure 2

The Figure 3 shows the deviation from the model implemented with the values of ε and σ reported in Table 2. The experimental data cover a wide range of temperature, from 273 K down to 150 K, i.e. down to Martian winter temperature. The model simulates both the structure I and II. At high temperature, the stable structure is sI. For example, at a temperature of 271K, the respective equilibrium pressure of sI and sII structures are 1.08 MPa and 1.38 MPa. But at lower temperature, especially in the range of temperature pertaining to Mars' winter period, there is an inversion of the stability. At a pressure of 0.6 kPa, the respective equilibrium temperatures of the structures sI and sII are 150K and 148.8K. Experimentally, the observed equilibrium temperature is 155 K (interpolated value from experimental data). It is the reason why Martian gas hydrate are suspected to be stable (Miller and Smythe, 1970)

Figure 3

Pure CH$_4$ hydrate

We optimised the kihara parameters from a set of 27 experimental results from Fray et al (2010), Yasuda and Ohmura (2008), Adisasmito et al. (1991) which cover a range of temperature from 145.75 to 286.4K and a pressure range from 2.4kPa to 10570kPa. The figure 4 plots the ε and σ values in the valley, and the corresponding deviation. The minimum deviation corresponds to values of ε and σ reported in Table 2.

Figure 4

Figure 5 shows the deviation from the model implemented with the values of ε and σ reported in Table 2. The experimental data covers a very wide range of temperature, from 273 K down to 80 K. The model fits with data for temperature below the ice point and deviates as the temperature decreases. In the temperature range close to 148 K, the model fits in between the data from Fray et al (2010) with an average deviation of 9.8%, and the data of Falabella and Vanpee (1974) with an average deviation of 19.75%. It must be said that the data sets from the two authors are significantly different, and that our model is in better agreement with the experimental corpus of Fray et al (2010).

Figure 5

Pure Ar hydrate

Figure 4 plots experimental data, and simulation from GasHyDyn software with Kihara parameters from Table 2. Data are the results of Saito and Kobayashi (1965) which have be found in Holder et al (1980), data from Barrer et Edge (1967), de Forcrand (1923) and Mohammadi and Richon (2011). The data from von Stackelberg (1949) are not reported because they appear not to be correct (Mohammadi and Richon, 2011). They cover a range of temperature from 283 K down to 90K. The deviation of the model is very good down to 138.7K with an average deviation of 2.59%. At temperature of 133.2K, deviation remains acceptable (10.9%) but diverges completely down to 115.9 K. In Martian conditions (down to 140-150 K), model and data are therefore in very good agreement.

Figure 6

Pure N₂ hydrate

In the literature, we can find one set of experimental data from Mohammadi and Richon (2010) and Kuhs et al (2000) at high temperature just under the ice formation conditions, and down to 250 K only. We added points at positive temperature to look at the model on the upper range of temperatures (from Jhaveri and Robinson, 1965). Model and data are plotted in Figure 3. The optimisation of the kihara parameters has been simplified because there is no data enough to distinguish the best value of ε and σ. For example, with CO_2 or CH_4, it can be observed from figure 2 or figure 4 that the deviation from model and experiments presents a clear minimum. We can retain the value of ε and at this minimum. But, for Nitrogen, there is no clear minimum. So, we retained the value of σ from Herri and Kwaterski (2011) and we optimized only ε. The result is given in Table 2.

The model fits pretty well with data of Jhaveri and Robinson (1965), above 0°C, and Mohammadi and Richon (2000), below 0°C. The change of the slope of the curve at the temperature of 0°C corresponds to a change of the phases in equilibrium. At positive temperature, the equilibrium is in between gas, liquid water and hydrate. Below 0°C, the equilibrium is in between Ice, Hydrate and Gas. At lower temperature, the model deviates very rapidly from the data of Kuhs et al (2000). So, it is difficult to predict how the model will simulate the nitrogen equilibrium in Martian conditions around 148 K. We need additional experimental data in Martian conditions to cross validate model and experiments. But we will see later that nitrogen only very slightly contributes to the stability of Martian hydrates in reason of a very poor integration in the hydrate structure. So, the precision of the model towards pure nitrogen hydrates is second order.

Figure 7

Intermediate conclusion

From a comparison between data and model in the temperature range around 148 K (corresponding to Martian conditions during winter above CO_2 ice caps), it can be seen that the model fits very well for argon and is acceptable for CO_2 (mean deviation of 12% in the range [151.5-171.5K] for sI structure, and 7% for sII structure) from the data of Miller and Smythe (1970)).

For pure methane hydrate, the model is between the data of Fray et al. (2010) and data Falabella and Vanpee (1974). From data of Fray et al. (2010), the model differs with a mean deviation of 25.7% at 145.8 K. The model differs from the data of Falabella and Vanpee (1974) with a deviation of 26.5% at 148.8 K and 22.5% at 159.9 K.

For N_2, we didn't find low temperature data enough to validate the Kihara parameters at low temperature.

1

2 ***Composite Martian hydrates***

3

4 We perform a simulation by assuming the presence of the dominating gases, only CO_2, N_2 and Ar.

5 Table 4 shows the results of the simulation in the range 139-161 K. It reports equilibrium pressure

6 of Structure I and Structure II hydrates. We can see that Structure II is the most stable structure to

7   be formed. The table 4 reports also the equilibrium pressure of pure CO_2 hydrate. We can see that

8   the mixture on Mars with 2.7% of N_2 and 2% of Ar gives a less stable hydrate which shifts the

9   equilibrium temperature, in a negligible manner. Secondly, if we look at the composition of the

10 hydrate phase, we can observe that the hydrate is practically one hundred percent CO_2 hydrate

11 with traces of nitrogen and argon. So, the chemical influence of secondary gases such as nitrogen

12 and argon is negligible because they do not participate in the structure. The shift in the equilibrium

13 temperature of Martian gas hydrates (CO_2 dominated but with 5 % of other gases) is principally

14 due to a decrease of the partial pressure of CO_2.

15

16   **Table 4**

17

18 Also, we can state that the equilibrium cannot be affected by the tertiary gases, at very low

19 concentrations, such as O_2 (1200±100 ppm), CO (700±200 ppm), H_2O (<1000 ppm, with an

20 average at 200 ppm), H_2 (20 ppm), O_3 (<0.2 ppm) and CH_4 (<50 ppb, with an average at 15 ppb).

21

22 For an atmospheric pressure on Mars of 0.6 kPa, the temperature at which the hydrates are stable is

23 149.3K (if SI structure is assumed) or 152.8K (if sII structure is assumed). Because winter surface

24 temperature on the south polar cap can reach 148K, the formation of CO_2 dominated clathrate is

25 possible during winter. Because summer temperature is much above 160 K in most regions of

26 Mars, most of these hydrates dissociate. Nevertheless, stable hydrates can survive during several

27 seasonal cycles at the top of or inside the south CO_2 ice polar cap, and transient hydrates can form

28 on seasonal polar caps during winter. So, we can postulate cycles of formation and dissociation of

29 hydrates associated with the winter/summer cycles, and the formation of stable hydrates over long

30 time scales on the south permanent polar cap.

Commentaire [ÉC1]: Veux-tu dire "with a slight shift of the equilibrium temperature"?

19

31

32 *The case of methane*

33

34 Methane is a very low concentration gas (15 ppb) and it has no influence on the equilibrium

35 (Pressure, Temperature) curve.

36

37 Table 5 reports the fractionation (or abundance fraction following the definition of Thomas et al,

38 2009) between gas and hydrate, that is the ratio between the molar fraction of a component in the

39 hydrate and the molar ratio of the same component in the gas.

40

41 At low Martian temperatures, methane composition in the hydrate structure SI is in the range from

42 12% to 18% (Table 5). Thomas et al (2009) reported a coefficient of 16.6% in condition similar to

43 ours (that means a very low methane concentration). The models give very similar results. If we

44 assume the structure II to be formed, the methane composition is higher, in the range from 26% to

45 35% (Table 6).

46

47 But, whatever the value of the abundance fraction (25-33% for structure II, 12-18% for structure

48 I), we can observe that methane is rather well encapsulated in the structure compared to nitrogen

49 or argon. As we said before, both gases do not effectively participate into the structure, first

50 because of their low concentration in the gas, but also due to their low affinity with the hydrate

51 structure. So, nitrogen and argon are not affected by the formation and dissociation of hydrate

52 between winter and summer. In comparison, methane, which is in a very low concentration, does

53 not disturb the hydrate equilibrium, but methane is affected by the formation of hydrate because it

54 can participate in the formation. Its abundance ratio (table 5) is one order of magnitude higher than

55   for nitrogen and argon. So, theoretically, methane in the gas phase is affected by the cycles of

56   formation and dissociation between winter and summer, and its concentration at the poles could be

57   different.

58

59   **Table 5**

60

61   **Discussion**

62

63   From a thermodynamical point of view, $CO_2/N_2/Ar/CH_4$ clathrate hydrates can form on both

64   seasonal polar caps and on the residual south polar cap. At seasonal scale, an upper limit of the

65   amount of CH_4 alternately trapped under hydrate form in the seasonal caps can be estimated by

66   assuming that all condensing/ sublimating water results in the formation of hydrate. Knowing that

67   only a fraction of condensing water is involved in hydrate formation, and that existing laboratory

68   experiments suggest that the kinetics of CO_2 hydrate formation is slow at low Martian

69   temperature, with time scales potentially several orders of magnitude above 1 Martian year

70   (Falenty et al., 2011), doing so results in a significant overestimation of the part of methane

71   seasonal variation due to hydrate formation/ dissociation. The amount of water exchanged between

72   seasonal polar caps is of the order of 10^{12} kg per Martian year (Richardson and Wilson, 2002).

73   Using an abundance ratio of CH_4 of 0.3 (average value between the abundance ratio in structure II

74   -Table 5- and the abundance ratio in structure I -Table 6-), a CH_4 concentration in hydrate three

75   times smaller than in the atmosphere, and assuming that all this water in involved in hydrate

76   formation, the corresponding exchanged mass of methane is $\approx 7\ 10^2$ kg. If clathrates are formed

77   during the massive condensation flow of CO_2 on the south polar cap during southern winter, the

78   mixing ratio of non-condensible gases (CH_4, N_2, Ar) is enhanced by a factor 4-5 at high southern

                                              21

79 latitudes due to the frictional effect of the CO_2 flow (Lefèvre and Forget, 2009). The previous

80 value could be therefore underestimated by a similar factor, with a very maximum of the CH_4

81 exchanged mass of 3 tons. The amount of methane in Mars atmosphere is of the order of 100 tons

82 (Geminale et al., 2011). It results that at most 1 %, or a few percents (up to 3 %), of the

83 atmospheric content of methane can be seasonally exchanged between the two hemispheres. The

84 true value is probably much smaller and the effect of the seasonally alternate formation of

85 clathrates on the CH_4 atmospheric content is therefore small, if not negligible.

86

87 It is thought that there is a net annual transfer of water from the north permanent polar cap to the

88 south permanent polar cap, due to very low temperatures on the south cap, which acts as a trap for

89 water vapor. The net water transfer rate is estimated to be ~10^{11} kg/yr, that is a thin water ice layer

90 of 1 mm thickness per year (Richardson and Wilson, 2002). The residence time of water in the

91 south permanent polar cap is large, typically several million years (time since the last obliquity

92 transition, see e. g. Levrard et al., 2004), and this water interacting with CO_2 ice can possibly

93 result in the formation of stable $CO_2/N_2/Ar/CH_4$ clathrate hydrates, progressively buried within the

94 caps. Because of the enhancement of the CH_4 mixing ratio by a factor 4-5 during southern winter

95 above the south polar cap, the effective abundance ratio of CH_4 with respect to the globally

96 averaged atmospheric CH_4 mixing ratio in these hydrates could be slightly larger than 1 (1.2-1.5),

97 with a CH_4/CO_2 ratio in the hydrate similar to, or slightly larger than, the atmospheric ratio.

98 Assuming that all condensing water is involved in hydrate formation, the time required to remove

99 the total atmospheric content would is the order of ~300 years. This value of the CH_4 lifetime with

100 respect to hydrate formation on the south permanent polar cap is probably much underestimated,

101 because only a fraction of the incorporated water ice is involved in hydrate formation, and

102 therefore of the same order as the photochemical lifetime of methane (300 yr, Krasnopolsky,

103   2006). Because the true lifetime of methane is much shorter (a few months or years, Lefèvre and

104   Forget, 2009), the net removal of methane by hydrate formation on the south polar cap may be

105   considered as a minor sink.

106

107   **Conclusions**

108

109   In this work, we have proposed a set of Kihara parameters to model pure gas clathrate hydrate

110   equilibrium in Martian winter conditions. We validated the model against experimental model and

111   obtained a good correlation, within a few percent in the best case (Ar) and 20-30% in the worst

112   case, for CO_2 and CH_4. The model for N_2 has not been validated because of the lack of data at very

113   low temperature. Also, we observed an inversion of the stability of the CO_2 hydrate which can be

114   probably a structure II in Martian winter conditions, and not a structure I as it is commonly

115   observed at higher temperature.

116

117   Then, we did a simulation of the Martian gas hydrate equilibrium and we found that the hydrate

118   can be considered as stable during the winter, and unstable during the summer. Even if methane

119   does not participate actively in the hydrate equilibrium because of its low relative abundance, its

120   concentration in the gas phase may be affected by the hydrate formation. The reason is that the

121   enclathratation of methane in the structure is not negligible (relative abundance of methane in the

122   hydrate is one third to one fourth of its value in the atmosphere). So, the concentration of methane

123   in the atmosphere may be *a priori* affected by the cycle of formation and dissociation of hydrates

124   between winter and summer if such cycles are existing.

125

126 We estimated an upper limit on the possible seasonal variation of methane generated by a

127 hypothetical alternate formation of hydrates on the seasonal polar caps. This upper limit is a few

128 percent of the atmospheric content of methane and can be considered as negligible. We similarly

129 proposed an upper limit for the lifetime of methane with respect to trapping on the south

130 permanent polar cap through hydrate formation, and found a minimum lifetime of 300 years, of the

131 same order as the photochemical lifetime and much longer than the presumably short lifetime of

132 six months derived from dynamical modelling. These mechanisms are therefore not expected to

133 play a significant role in the present dynamics of Martian methane, although they could have been

134 significant at early times, when the atmosphere contained more methane.

135

136 Interestingly, hypothesized clathrate hydrates trapped in the permanent south polar cap could

137 include methane in relative proportions between 0.3 (equilibrium value) and 1.5 (due to frictional

138 enhancement by CO_2 condensing flow) times the average global atmospheric ratio. Searching for

139 the spectral signatures of clathrate hydrates on the caps and, if detectable, of inhomogeneities of

140 the CH_4 mixing ratio in possible local atmospheric plumes forming during the sublimation of polar

141 hydrate pockets in spectroscopic data from existing (Mars Express, MRO) and future (TGO-

142 Exomars) missions is clearly an interesting challenge of Mars science and astrobiology.

143

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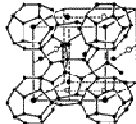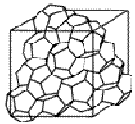
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Tables :

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 (ν_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=1.1956 (3)		a=1.7315 (4)	
Cell volume (nm³)	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).

Table 2
Kihara parameters optimized during this work

	$\dfrac{\varepsilon}{k}$	a	σ	
CO_2	178.21	0.6805	2.873	This work
CH_4	166.36	0.3834	3.05	
N_2	133.13	0.3526	3.0993	
Ar	174.14	0.184	2.9434	
CO_2	171.41	0.6805	2.9830	Herri et al, 2011
CH_4	158.71	0.3834	3.1503	
N_2	138.22	0.3526	3.0993	

Table 3
Reference state parameters

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

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

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

Table 4
Equilibirum conditions of pure CO_2 and Martian gas hydrates

	Pure CO_2 Hydrate	CO_2-Ar-N_2 Hydrate Gas composition (0.953CO_2, 0.026Ar, 0.020N_2)					
T (K)	Equilibrium Pressure (Pa)				Hydrate composition		
	SII structure	SII structure	SI structure	θ	CO_2	N_2(x10^3)	Ar(x10^3)
139	96	99	202	0.962	0.999	0.15	0.52
140	111	117	226	0.963	0.999	0.16	0.54
141	129	135	252	0.963	0.999	0.16	0.56
142	147	154	280	0.963	0.999	0.17	0.59
143	169	176	309	0.964	0.999	0.18	0.61
144	192	202	347	0.964	0.999	0.18	0.64
145	219	230	385	0.964	0.999	0.19	0.67
146	249	260	427	0.964	0.999	0.20	0.70
147	283	296	474	0.964	0.999	0.20	0.73
148	321	336	524	0.964	0.999	0.21	0.75
149	362	377	580	0.964	0.999	0.22	0.79
150	410	429	640	0.965	0.999	0.23	0.82
151	462	484	708	0.965	0.999	0.23	0.85
152	519	545	781	0.965	0.999	0.24	0.88
153	585	613	860	0.965	0.999	0.25	0.91
154	657	688	946	0.965	0.999	0.26	0.95
155	736	771	1039	0.965	0.999	0.26	0.98
156	824	863	1145	0.965	0.999	0.27	1.02
157	921	964	1255	0.965	0.999	0.28	1.06
158	1027	1064	1373	0.965	0.999	0.29	1.09
159	1145	1198	1511	0.965	0.999	0.30	1.13
160	1274	1333	1654	0.965	0.999	0.31	1.17
161	1410	1481	1809	0.965	0.998	0.32	1.21

Table 5
Abundance fraction of component in hydrate versus component in gas
SII is supposed

Equilibrium condition Gas= 95,3% CO_2, 2% Ar, 2.7% N_2, 15 ppb CH_4		Abundance ration =xi/fi xi : composition of i in the hydrate fi : composition of i in the gas SII is supposed			
T (K)	P (kPa)	CO_2	N_2	Ar	CH_4
139	99.0	1.048	0.008	0.020	0.262
140	117.3	1.048	0.008	0.021	0.266
141	134.7	1.048	0.008	0.022	0.270
142	154.4	1.047	0.008	0.023	0.274
143	176.3	1.047	0.009	0.024	0.278
144	201.6	1.047	0.009	0.025	0.282
145	229.6	1.047	0.009	0.026	0.286
146	259.7	1.047	0.010	0.027	0.291
147	296.5	1.047	0.010	0.028	0.295
148	335.5	1.047	0.011	0.029	0.299
149	377.2	1.047	0.011	0.030	0.303
150	429.4	1.047	0.011	0.031	0.307
151	484.3	1.047	0.012	0.033	0.311
152	545.4	1.047	0.012	0.034	0.315
153	613.0	1.047	0.012	0.035	0.319
154	688.0	1.047	0.013	0.036	0.323
155	771.1	1.047	0.013	0.038	0.327
156	862.7	1.047	0.014	0.039	0.331
157	964.0	1.047	0.014	0.041	0.335
158	1063.7	1.047	0.014	0.042	0.339
159	1198.2	1.047	0.015	0.044	0.343
160	1332.7	1.047	0.015	0.045	0.347
161	1481.2	1.047	0.016	0.047	0.351

Table 6
Abundance fraction of component in hydrate versus component in gas
SI is supposed

Equilibrium condition Gas= 95,3% CO_2, 2% Ar, 2.7% N_2, 15 ppb CH_4		Abundance ration =xi/fi xi : composition of i in the hydrate fi : composition of i in the gas SI is supposed			
T (K)	P (kPa)	CO_2	N_2	Ar	CH_4
139	202.2	1.048	0.003	0.005	0.126
140	225.7	1.048	0.004	0.005	0.129
141	251.6	1.048	0.004	0.006	0.131
142	279.8	1.048	0.004	0.006	0.134
143	309.2	1.048	0.004	0.006	0.137
144	347.1	1.048	0.004	0.006	0.139
145	385.4	1.048	0.005	0.007	0.142
146	427.5	1.048	0.005	0.007	0.144
147	473.9	1.048	0.005	0.007	0.147
148	524.1	1.048	0.005	0.008	0.149
149	579.8	1.048	0.005	0.008	0.152
150	640.1	1.048	0.006	0.009	0.155
151	708.1	1.048	0.006	0.009	0.157
152	780.8	1.048	0.006	0.009	0.160
153	860.4	1.048	0.006	0.010	0.163
154	946.2	1.048	0.006	0.010	0.165
155	1039.0	1.048	0.007	0.011	0.168
156	1144.9	1.048	0.007	0.011	0.171
157	1255.4	1.048	0.007	0.012	0.173
158	1372.9	1.048	0.008	0.012	0.176
159	1510.5	1.048	0.008	0.013	0.179
160	1654.3	1.048	0.008	0.013	0.181
161	1808.9	1.048	0.008	0.014	0.184

Figure captions :

Figure 1: Deviation between experimental equilibrium data of pure CO_2 hydrate and model versus ε/k and σ. a value is taken from Table 2. Data are taken fromYasuda and Ohmura (2008), Adisasmito et al. (1991), Falabella (1975), Miller and Smythe (1970) which cover a range of temperature from 151.52K to 282.9K and a pressure range from 0.535kPa to 4370kPa.

Figure 2: ε/k versus σ at the minimum deviation with experimental data. a value is taken from Table 2. Pressure and temperature equilibrium data for CO_2 hydrate are taken fromYasuda and Ohmura (2008), Adisasmito et al. (1991), Falabella (1975), Miller and Smythe (1970) which cover a range of temperature from 151.52K to 282.9K and a pressure range from 0.535kPa to 4370kPa.

Figure 3 : Equilibrium pressure of pure CO_2 gas hydrate at low temperature down to the Martian winter Martian conditions (148K ±10K)

Figure 4: ε/k versus σ at the minimum deviation with experimental data. a value is taken from Table 2. Pressure and temperature equilibrium data for CH_4 hydrate are taken from Fray et al (2010), Yasuda and Ohmura (2008), Adisasmito et al. (1991) which cover a range of temperature from 145.75 to 286.4K and a pressure range from 2.4kPa to 10570kPa

Figure 5 : Equilibrium pressure of pure CH4 gas hydrate at low temperature down to the Martian winter Martian conditions (148K ± 5K)

Figure 6 : Equilibrium pressure of pure Argon gas hydrate at low temperature (283-263K and 150-90K)

Figure 7 : Equilibrium pressure of pure Nitrogen gas hydrate in a limited range of temperature (273 down to 250 K)