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Jean-Michel Herri, Michel Cournil, Eric Chassefière

THERMODYNAMIC MODELLING OF CLATHRATE HYDRATES IN THE ATMOSPHERE OF MARS

Jean-Michel Herri[1*], Michel Cournil[1], Eric Chassefière[2]
Centre SPIN, École Nationale Supérieure des Mines de Saint-Étienne [1]
158, cours Fauriel, 42023 SAINT-ÉTIENNE, France
IDES, University Paris-Sud, Bat. 504. 91405 ORSAY Cedex, France [2]

ABSTRACT

The papers deals with the stability at low temperature and low pressure in the atmospheric conditions of March, that means a gas composition mainly dominated by CO2 plus low concentration of Argon and Nitrogen and traces of gases as methane. The paper is mainly based on the data compilation from Fray et al (2011) for pure gases equilibriums. We fit the classical van der Waals approach to compare deviation. It reveals to be acceptable and allows to simulate a Martian gas of CO_2 dominated (95.3%) plus nitrogen (2.7%) and Argon (2%). The hydrate reveals to be a CO2 based hydrate which is unstable during Mars summer and stable during Mars winter time (at temperature below 154K). The proportion of methane in the hydrate is evaluated and reveals to be one fourth of the composition of the gas phase.

Keywords: gas hydrates, kinetic inhibitors

INTRODUCTION

The discovery of methane in the atmosphere of Mars, at first by the spectrometer PFS of the ESA probe Mars – Express (Formisano et al., 2009) then more recently from the telescope of Hawaii (Mumma et al., 2009), arouse a very big interest in planetology and exobiological communities.

The origin of this methane is not known and can be attributed to the serpentinisation during current or past hydrothermal systems, and/or be attributed to the presence of methanogenic bacteria (Chassefière and Leblanc, 2011).

A multidisciplinary group of several laboratories from the Universities of Orsay and Versailles Saint-Quentin (IDES, IAS, LATMOS), in association with a team of the École Nationale Supérieure des Mines de Saint-Etienne (LPMG) and the laboratory UTINAM (Besançon) began the study of the clathrates of methane in Martian conditions. This study, financed by the interdisciplinary program EPOV (Planet Environments and Origins of the Life), participates to the preparation of the mission ESA-NASA Exomars Gas Trace Orbiter (2016). It concerns four different but complementary domains of research : i) Question of the origin of the methane and its circulation in the systems sediment – cryosphere- atmosphere, as well as of its reservoirs of storage; ii) the modelling of the domains of stability (Pressure, Temperature) of pure and mixed clathrates in Martian conditions; iii) the research of the sources of methane on the surface via the observation of methane (gaseous and solid) and of tracers of the degassing (radon); iv) the consequences of the existence of methane on our understanding of the climatic evolution and geo-morphology of Mars; v) the link between mineral and biological production of methane in the hydrothermal systems.

The paper deals with the second topic and presents a modelling of the (Pressure-Temperature) equilibrium curve in the atmosphere of Mars. The paper compiles experimental data from literature (Fray et al, 2010) and fits a model (Herri et al, 2010) based on van der Waals approach. For pure gases and in winter Martian conditions (temperature evaluated in the range of 140-160K), 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 reveals to be a

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[*] Corresponding author: Phone: +33 (0)4 77 42 02 92, Fax : +33 (0)4 77 42 96 94 E-mail: herri@emse.fr

CO2 based hydrate which is stable at temperature below 154K if pressure is supposed to be 0.6 kPa. If pressure is supposed to be 0.7 kPa (Thomas et al, 2009), the hydrate is stable at temperature below 156K. It signifies the Martian gas hydrate is strongly suspected to be stable during the winter season. The proportion of methane in the hydrate is evaluated and compared to the evaluation performed by Thomas et al, 2009.

Introduction

The van der Waals and Platteeuw (1959) model describes the equilibrium of hydrate phases by means of an 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 understanding 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 presented 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 was not only classical (Pressure,Temperature) equilibrium curves but also the envelope curves for gases mixtures consisting in (Pressure, Temperature, gas composition and hydrate compotion) 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 retain these parameters to simulate hydrate equilibrium. In Herri et al (2011), the Kihara parameters have been optimized in (pressure – temperature) conditions on which we can have a maximum of experimental data from literature, that means principally the earth ambient temperature 273-293 K and pressure of the order of magnitude of 1 to some tens of MPa. The ambient Martian conditions are very different. Pressure is around 0.6-0.7 kPa. In winter period, on the southern permanent CO_2 ice polar cap, the temperature can be 148K (temperature of CO_2 anti sublimation at 0.6 kPa). During the summer period, at low altitude and sunny time, temperature can reach 273 K exceptionally.

So, the possibility to extrapolate the van der Waals and Platteeuw model from Earth condition to Martian condition need to be questioned. In this paper, we validate the model against available data of pure gas hydrate around the Martian conditions. Data essentially comes from the compilation of Fray et al (2010), plus rare additional data.

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 polyhedra cavities called 5^{12}, $5^{12}6^2$, $5^{12}6^4$, $4^3 5^6 6^3$ 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). On Table 1 are described more precisely the SI and SII structure that can be only formed in respect to the nature of the Martian gases.

Table 1
Structure of SI and SII gas Hydrates
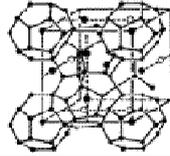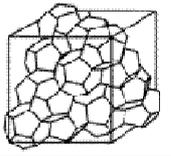
Cavity	SI		SII	
	5^{12}	$5^{12}6^2$	5^{12}	$5^{12}6^4$
Type of cavity (j. indexing number)	1	2	1	3
Number of cavities (n_i)	2	6	16	8
Average cavity radius (nm) (1)	0.395	0.433	0.391	0.473
Variation in radius, % (2)	3.4	14.4	5.5	1.73
Coordination number	20	24	20	28
Number of water molecules	46		136	
Cell parameters (nm)	a=11.955 (3)		a=17.3 5 (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).

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.

$$\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta} \tag{1}$$

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

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

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

$$\Delta\mu_w^{H-\beta} = RT\sum_i v_i \ln\left(1 - \sum_j \theta_j^i\right) \tag{2}$$

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:

$$\Delta\mu_w^{H-\beta} = RT\sum_i v_i \ln\left(1 - \sum_j C_j^i f_j(T,P)\right) \tag{3}$$

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:

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

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:

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

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

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.

Table 2
Kihara parameters

	$\frac{\varepsilon}{k}$	a	σ	
CO_2	171.41	0.6805	2.9830	This work,
CH_4	158.71	0.3834	3.1503	modified from
N_2	133.13	0.3526	3.0993	Herri *et al*, 2011
Ar	174.14	0.184	2.9434	This work, modified from Parrish and Prausnitz, 1972

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 vapor 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 $\Delta h_w^{L-\beta}\big|_{P^0}$ 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 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
$\Delta v_w^{L-\beta}\big|_{T^0}$	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

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

Equilibrium

Equilibrium is achieved as equality of $\Delta\mu_w^{H-\beta} = \Delta\mu_w^{L-\beta}$ 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 (P,T, gas composition, hydrate composition) experimental data base (more details in Herri et al, 2011).

Data Base

The data base of GasHyDyn Sofware has been completed with the data at low temperature compiled in the paper of Fray et al, 2010 for methane and CO2 clathrate below the ice points. Very few data can be found for N2 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 148.8 to 291 K (in Holder et al, 1980, original data from Saito S., and Kobayashi,1965, and original data from Barrer and Edge , 1967).

Simulation of Martian Hydrates

The equilibrium is first order governed by the dominating gas (CO2, 95.7%) and secondly affected by second order constituents (N2, 2.7%, and Ar, 2%). It is not affected by very low concentration components such as O2 (1200±100 ppm), CO (700±200 ppm), H2O (<1000 ppm with an average at 200 ppm), H2 (20 ppm), and O3 (<0.2 ppm)) and CH$_4$ (<50ppb with an average at 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.

Simulation of pure gas equilibrium at Martian condition

Pure Argon hydrates: Figure 2 plots experimental data and simulation from GasHyDyn software. Data compiled from Holder et al (1980) are the results of Saito and Kobayashi (1965) and Barrer et Edge (1967) and covers a range temperature from 283 K down to 150K. The deviation of the model is very good, 4% maximum. At 150K, the experimental equilibrium pressure of Pure Argon hydrate is 0.1 MPa to be compared to the partial pressure on Mars which is 2 % of 0.6 kPa. Pure Argon hydrate can not be stable on Mars.
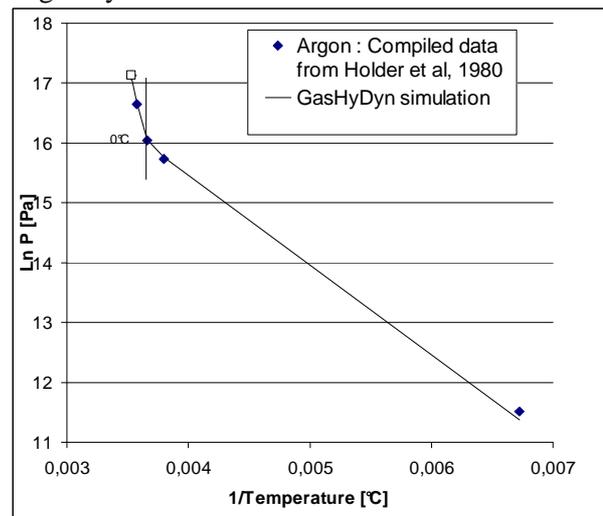
Figure 1
Pure Argon gas hydrate at low temperature down to the Martian winter Martian conditions (148K +- 10K)

Pure CO2 hydrates: Figure 1 plots experimental data and simulation from GasHyDyn software. The experimental data covers a wide range of temperature, from 273K down to 150K, i.e. down to Martian winter temperature. The deviation of the simulation increases from 1% (at 273K) to 25%(162.8K) and decreases to 17%(151,5K). If the Martian atmosphere (Pressure of 6kPa) would have been 100% CO2, the temperature below which the CO2 hydrate would be stable is 153 K (model) or 155 K (experimental data). It is the reason Martian gas hydrate have been suspected to be stable (Miller and Smythe, 1970)
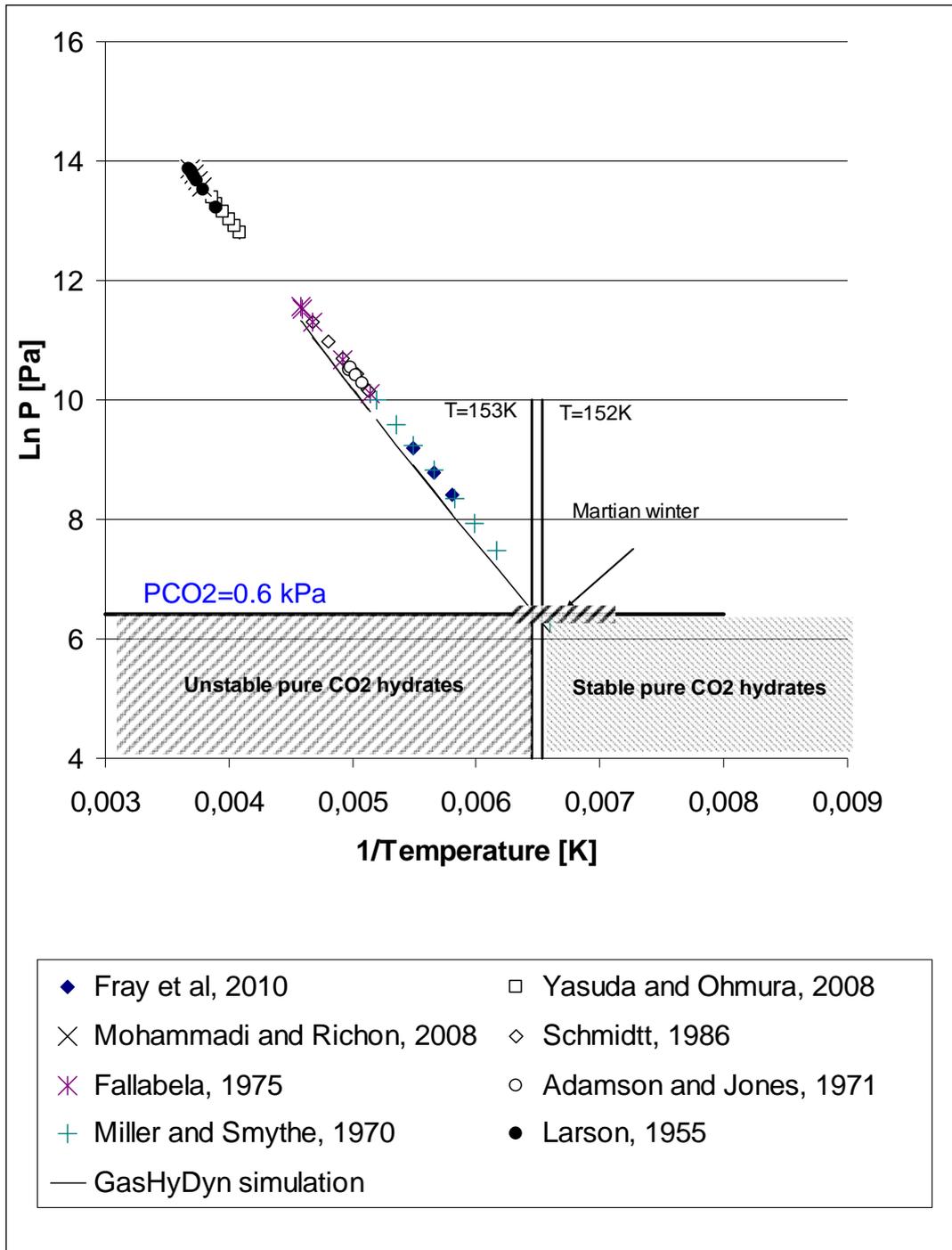

Figure 1
Pure CO2 gas hydrate at low temperature down to the Martian winter Martian conditions (148K +- 10K)

Pure N2 hydrate: in the literature, we have one set of data from Mohammadi and Richon (2010) and Khus et al (2000) at high temperature just under the ice formation conditions, down to 250 K only. We added point at positive temperature to look at the model on the larger range of 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 at Martian conditions around 148K. Like the other gases, we need experimental data at Martian conditions to cross validate model and experiments. But, we will see later that Nitrogen very slightly contributes to the stability of Martian hydrates in reason of a very poor integration in the hydrate structure, and whatever it is not stable as a pure component hydrate at Martian conditions. So, the precision of the model towards pure Nitrogen hydrates is second order.

Pure CH4 Hydrate: the experimental data covers a very wide range of temperature, from 273 K down to 80K. Figure 4 plots the data and model.
As for previous gases (CO2, N2, Ar), model fits with data for temperature below the ice point and deviates as the temperature decreases. In the range temperature close to 148K, the model fits very

well with the data from Fray et al (2011) with a deviation of 3-4%, but deviates from the data of Falabella and Vanpee (1974) with a deviation of 42%. It can be said that the data sets from the two authors are clearly different and our model fits better with experimental corpus of Fray et al (2011).

Intermediate conclusion: from comparison between data and model in the temperature range around 148K (which is supposed to be a temperature close to the winter temperature at Mars surface), we can observe the model fits very well for rare gas Argon and is acceptable for CO2 (mean deviation of 17% at 151.5K from the data of Miller and Smythe (1970).
For pure methane hydrate, the model fits will with the data from Fray et al (2011) with a mean deviation of 3.5% at 145.8K. The model differs from the data of Falabella and Vanpee (1974) with a deviation of 42.6% at 148.8K and 39% at 159.9K.
For N2, we didn't find low temperature data enough to validate the Kihara parameters at low temperature.
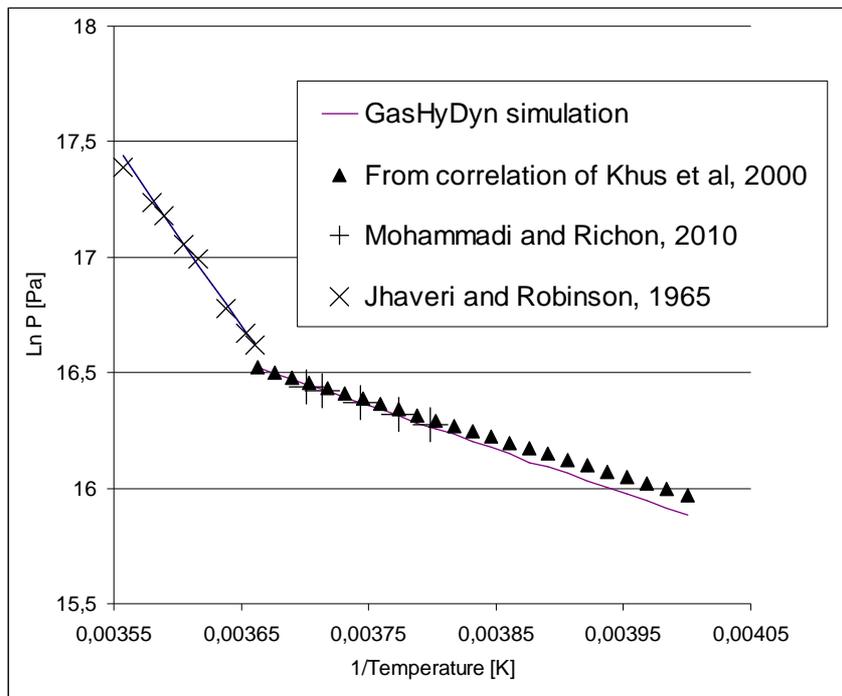
Figure 3
Pure Nitrogen gas hydrate in a limited range of temperature (273 down to 250 K)
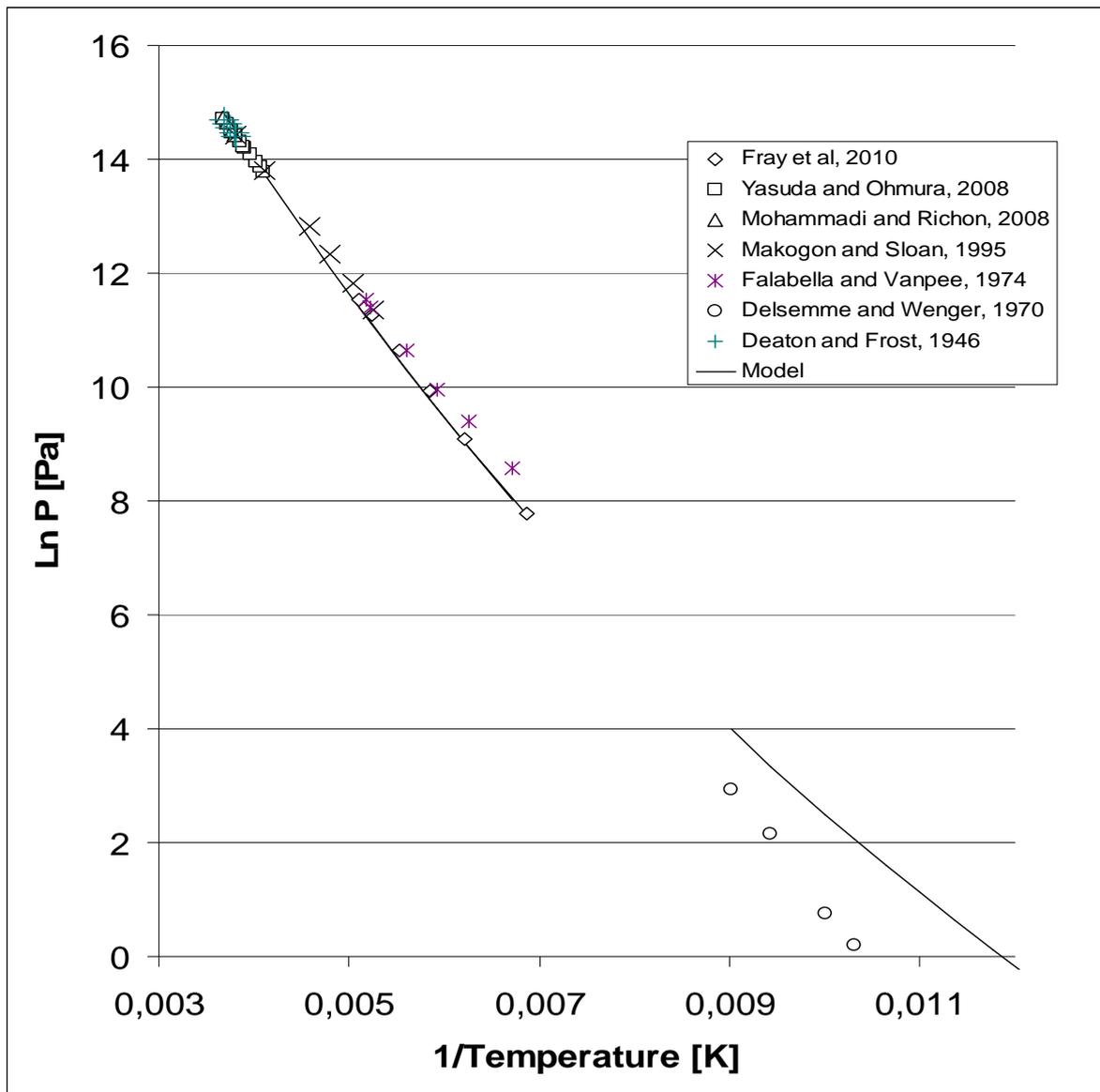
Figure 4

Pure CH4 gas hydrate at low temperature down to the Martian winter Martian conditions (148K +- 10K)

Martian hydrates: 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) Pressure is around 0.6 kPa. In winter period, on the CO2 solid crust, the temperature can be 148K (temperature of CO2 anti sublimation at 0.6kPa). During the summer period, at low altitude and sunny time, temperature can rise 273 K exceptionally.

Low concentration compounds are supposed to not affect the hydrate equilibrium. This point will be validated further.

So, we do a simulation by assuming only CO_2, N_2 and A_r.

Table 4 reports simulation in the range 139-161K. It reports equilibrium pressure of Structure I and Structure II hydrates. We can see that Structure I is the most stable structure to be formed. The table 4 reports also the equilibrium pressure of pure CO2 hydrate. We can see that the mixture on Mars with 2.7% of N2 and 2% of Ar gives a less stable hydrate which shifts the equilibrium temperature at 600 Pa from 155K to 154K, that means a

negligible influence. Secondly, if we look at the composition of the hydrate phase, we can observe that the hydrate is practically one hundred percent CO2 hydrate with traces of Nitrogen and Argon. So, the chemical influence of secondary gases such as Nitrogen and Ar is negligible because they do not participate to the structure. So, the shift in the equilibrium temperature of Martian gas hydrate (CO2 dominated but with 5 % of other gases) is only due to a depletion of the partial pressure in CO2.

Also, we can affirm that the equilibrium can not be affected by the tertiary gases which are in a two much low concentration such as O2 (1200±100 ppm), CO (700±200 ppm), H2O (<1000 ppm with an average at 200 ppm), H2 (20 ppm), and O3 (<0.2 ppm)) and CH_4 (<50ppb with an average at 15 ppb).

Atmospheric pressure on Mars is about 600 Pa. Temperature at which the hydrates are stable is 155-156K. Because winter temperature can be below (around 148K), it can be said that the hydrate can form during winter. Because summer temperature are much above 160 K in most regions of Mars, except on the permanent south polar cap, most of these hydrates dissociate. Nevertheless, stable hydrates can survive during several seasonal cycles at the top or inside the south CO2 ice polar cap. So, we can postulate cycles of formation and dissociation of hydrates associated with the winter/summer cycles.

What about methane ?
Methane is a very low concentration gas (15 ppb) and it has not any influence on the equilibrium (Pressure, Temperature curve). At 154 K, the equilibrium pressure 597 kPa without methane, and it is the same value with 15 ppb methane in the gas.

Table 6 reports the fractionation (or abundance fraction in the definition of Thomas et al, 2009) on gases between gas and hydrate.

At low temperature of March (around 148 K), methane composition in the hydrate structure is between one third to one fourth of the composition of methane in the gas phase. Thomas et al (2011) reports a coefficient of 0.166 in condition similar to us (that means a very low methane concentration). The difference is essentially due to a different choice of the Kihara Parameters, but we can not say more because Thomas et al (2009) do not present a validation of their Kihara parameters versus a modelling of

(Pressure/temperature) diagram of pure gases. But, whatever the value of the abundance fraction (25-33% in our case, 16% for Thomas et al, 2009), we can observe that methane is rather well enclathred in the structure compared to Nitrogen or Argon. As we said before, both of these gases do not participate at all to the structure, firstly because of their low concentration in the gas, but also because of their low affinity to the hydrate structure. So, Nitrogen and Ar are not affected by the formation and dissociation of hydrate between winter and summer. In comparison, methane which is in a very low concentration does not perturb the hydrate equilibrium, but methane is affected by the formation of hydrate because he can participate to the formation. It abundance ratio (table 5) is one order of magnitude higher than for Nitrogen and Argon. So, theoretically, methane in the gas phase is affected by the cycles of formation and dissociation between winter and summer, and its concentration at poles could be different.

Conclusion:
In these work, we have proposed a set of Kihara parameters to model pure gas hydrate equilibria at Martian condition. We validate the model against experimental model and we observe a good correlation of some percent in the better case (Ar) and inferior to 20-25% of deviation in the worst case (CO2 and CH4). N2 has not been validated in reason of the lack of data at very low temperature. Then, we did a simulation of the Martian gas hydrate equilibrium and we found that the hydrate can be considered as stable during the winter, and unstable during the summer. Even if methane does not participate actively at the hydrate equilibrium because its concentration in the gas phase is too much low, inversely the methane gas concentration must be affected by the hydrate equilibrium. The reason is the enclathratation of methane in the structure is not negligible (abundance of methane in the hydrate is about one third or one fourth of the gas composition in the atmosphere). So, variation of methane in the atmosphere could be affected by the cycle of formation and dissociation of hydrates between winter and summer if such cycles are existing.

Table 4
Equilibirum conditions of pure CO2 and Martian gas hydrates

T (K)	Pure CO_2 Hydrate		CO_2-Ar-N_2 Hydrate Gas composition (0.953CO_2, 0.026Ar, 0.020N_2)				
	Equilibrium Pressure (Pa)				Hydrate composition		
	SI structure	SII structure	SI structure	θ	CO2	N2($\times 10^3$)	Ar($\times 10^3$)
139	108	560	114	0.991	0.999	0.271	0.561
141	137	727	144	0.990	0.999	0.291	0.606
143	173	938	181	0.989	0.999	0.312	0.654
145	217	1200	228	0.988	0.999	0.335	0.703
146	243	1348	254	0.987	0.999	0.346	0.729
148	297	1715	317	0.986	0.999	0.370	0.782
149	337	1923	354	0.986	0.999	0.382	0.809
150	376	2158	393	0.985	0.999	0.394	0.837
151	417	2415	438	0.985	0.999	0.407	0.865
153	515	3013	538	0.984	0.999	0.432	0.922
154	571	3352	597	0.983	0.999	0.446	0.952
155	631	3735	662	0.982	0.999	0.459	0.982
156	699	4150	730	0.982	0.999	0.473	1.013
157	767	4601	809	0.981	0.998	0.487	1.044
158	841	5102	894	0.981	0.998	0.501	1.076
160	1036	6234	1086	0.979	0.998	0.530	1.141
161	1141	6889	1195	0.979	0.998	0.544	1.174

Table 5
Abundance fraction of component in hydrate versus component in gas

Equilibrium condition Gas= 97,4% CO_2, 2,7%N_2, 2% Ar, 15 ppb CH_4		Abundance ration =xi/fi xi : composition of i in the hydrate fi : composition of i in the gas			
T (K)	P (kPa)	CO2	N2	Ar	CH_4
139	113,6	1,048	0,010	0,028	0,270
143	181,5	1,048	0,012	0,033	0,281
147	284,5	1,048	0,013	0,038	0,291
150	393,5	1,048	0,015	0,042	0,299
151	437,5	1,048	0,015	0,043	0,302
154	596,8	1,048	0,017	0,048	0,310
155	661,7	1,048	0,017	0,049	0,313
157	809,4	1,048	0,018	0,052	0,318
158	893,6	1,047	0,019	0,054	0,320
159	985,6	1,047	0,019	0,056	0,323
160	1086,1	1,047	0,020	0,057	0,326

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