Variability of the methane trapping in martian subsurface clathrate hydrates

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Abstract

Recent observations have evidenced traces of methane (CH$_4$) heterogeneously distributed in the martian atmosphere. However, because the lifetime of CH$_4$ in the atmosphere of Mars is estimated to be around 300–600 years on the basis of photochemistry, its release from a subsurface reservoir or an active primary source of methane have been invoked in the recent literature. Among the existing scenarios, it has been proposed that clathrate hydrates located in the near subsurface of Mars could be at the origin of the small quantities of the detected CH$_4$. Here, we accurately determine the composition of these clathrate hydrates, as a function of temperature and gas phase composition, by using a hybrid statistical thermodynamic model based on experimental data. Compared to other recent works, our model allows us to calculate the composition of clathrate hydrates formed from a more plausible composition of the martian atmosphere by considering its main compounds, i.e. carbon dioxide, nitrogen and argon, together with methane. Besides, because there is no low temperature restriction in our model, we are able to determine the composition of clathrate hydrates formed at temperatures corresponding to the extreme ones measured in the polar caps. Our results show that methane enriched clathrate hydrates could be stable in the subsurface of Mars only if a primitive CH$_4$-rich atmosphere has existed or if a subsurface source of CH$_4$ has been (or is still) present.

Key words: Mars; Clathrate hydrates; Atmosphere; Methane

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1 Introduction

The Planetary Fourier Spectrometer (PFS) onboard the Mars Express spacecraft has detected $\sim 10$ parts per billion by volume (ppbv) of methane in the atmosphere of Mars (Formisano et al., 2004). Comparable abundances have been reported by Mumma et al. (2003), by Krasnopolsky et al. (2004), and very recently by Villanueva et al. (2008) from ground-based observations. Because the photochemical mean lifetime of the atmospheric methane is about 300–600 years (Krasnopolsky et al., 2004; Formisano et al., 2004), its release from a subsurface reservoir or an active primary source of methane have been invoked in the recent literature. It has thus been suggested that the methane observed on Mars could be of biogenic origin and would originate from organisms living in the near subsurface (Formisano et al., 2004; Krasnopolsky et al., 2004; Krasnopolsky, 2006) or that the olivine hydration in the martian regolith or crust could be a major methane source (Oze and Sharma, 2005). Alternatively, it has been proposed that the methane observed on Mars could be produced from photolysis of water in the presence of CO (Bar-Nun and Dimitrov, 2006).

The atmospheric methane of Mars could also be tied to the possible presence of methane clathrate hydrates that decompose in the near-subsurface (Prieto-Ballesteros et al., 2006; Chastain and Chevrier, 2007). In this case, clathrate hydrates don’t bring any constraint on the origin of the martian methane. Indeed, their ability to retain methane over long timescales make them a secondary reservoir which can be filled either by ancient or by current methane sources (Prieto-Ballesteros et al., 2006; Chastain and Chevrier, 2007). In this context, the stability of methane clathrate hydrates under martian conditions has been explored by Chastain and Chevrier (2007) (hereafter CC07) with the use of the program CSMHYD developed by Sloan (1998). From these calculations, CC07 determined the plausible composition of methane clathrate hydrates that could be located in the martian crust or in the polar caps. They also discussed the possible sources that may be at the origin of these clathrate hydrates.

However, these authors only considered the formation of binary CO$_2$-CH$_4$ clathrate hydrates from the martian atmosphere, due to the limited list of available molecules in the CSMHYD program. With a fractional abundance of 95\%, carbon dioxide is the main atmospheric compound, but other molecules such as nitrogen and argon, whose abundances reach $\sim 2.7$ and 1.6 \% respectively (Moroz, 1998), have been neglected in the composition and stability calculations of clathrate hydrates by CC07. As shown by Thomas et al. (2007, 2008) in the case of Titan, minor compounds can strongly affect the composition of clathrate hydrates formed from the atmospheric gas phase and also their temperature dependence. Moreover, because the CSMHYD code is not
suitable below $\sim 171$ K for CO$_2$-CH$_4$ gas mixtures relevant to the atmospheric composition of Mars, CC07 did not calculate the composition of clathrate hydrates possibly formed in the polar caps where the in situ temperature can decrease down to $\sim 130$ K (Kieffer et al., 2001).

In the present work, we reinvestigate the assumptions of CC07 and determine more accurately the composition of clathrate hydrates that may form in the near subsurface of Mars as a function of temperature and gas phase composition, by using a statistical thermodynamic model based on experimental data and on the original work of van der Waals and Platteeuw (1959). Compared to the work of CC07, our model allows us to calculate the composition of clathrate hydrates formed from a more plausible composition of the martian atmosphere by considering its main compounds, i.e. carbon dioxide, nitrogen and argon, together with methane. Besides, because there is no low temperature restriction in our model, we are able to determine the composition of clathrate hydrates formed at temperatures corresponding to the extreme ones measured in the polar caps.

2 Theoretical background

2.1 Model

To calculate the relative abundance of CH$_4$ incorporated in clathrate hydrates on Mars, we used the same approach as in our previous studies devoted to the trapping of noble gases by clathrate hydrates on Titan (Thomas et al., 2007, 2008). This approach is based on the statistical model developed by van der Waals and Platteeuw (1959) and it is similar to the one proposed by Sloan (1998) in the CSMHYD program. However, it differs from this latter approach by the use of experimentally determined dissociation curves in our code instead of calculated dissociation pressures (Thomas et al., 2008). This allows us to determine the relative abundances in clathrate hydrates down to very low temperatures whereas the CSMHYD program is for example limited to $\sim 171$ K for the clathrate hydrates considered here.

In order to validate the calculations performed in the present study, we have compared the results issued from our approach to those obtained using the CSMHYD program when considering gas phases containing CH$_4$ and CO$_2$ in different initial abundances. As an illustration, we present on Figure 1 the relative abundances of methane in mixed CO$_2$/CH$_4$ clathrate hydrates as calculated with our code by considering several initial abundances of CH$_4$ in the gas phase (0.01%, 0.1%, 1%, 10%, 20%, 50% or 90% (the relative abundance of CO$_2$ in each case is determined such as $x_{CH_4} + x_{CO_2} = 1$). Figure 1 clearly shows
that CH$_4$ abundances in clathrate hydrates obtained from our program (full line) using the Kihara parameters and cage geometries given by Sloan (1998) fit very well those obtained with the CSMHYD program (crosses) down to 171 K, that is in the range for which this program converges. This comparison demonstrates the validity of our approach and illustrates its advantage for characterizing clathrate hydrates at temperatures outside the range accessible to the CSMHYD program.

2.2 Accuracy of the potential parameters

The calculations of the relative abundances of a guest species trapped in clathrate hydrates depend both on the structural characteristics of the clathrate hydrate under consideration and on the accuracy of the corresponding interactions between the trapped molecule and the water cage (Thomas et al., 2008). As a consequence, the accuracy of the present calculations strongly depends on the choice of the parameters of the Kihara potential.

In our previous study (Thomas et al., 2008), we have shown that an appropriate set of parameters for clathrate hydrate studies on Titan has been given by Parrish and Prausnitz (1972), in which potential and structural parameters have been self-consistently determined on experimentally measured clathrate hydrate properties.

To check the accuracy of these parameters in the present application on Mars, we have compared the relative abundances obtained with the Kihara parameters given by Sloan (1998) (same as in the CSMHYD program) to those calculated using the Kihara parameters given by Parrish and Prausnitz (1972) (Table 1). Surprisingly, calculations performed with the parameters from Parrish and Prausnitz (1972) lead to results at the opposite of those obtained with the parameters given by Sloan (1998). Indeed, the parameters from Parrish and Prausnitz (1972) lead to a better trapping when the clathrate hydrates form at low temperatures than when they form at high temperatures. This appears very puzzling given that parameters from Parrish and Prausnitz (1972) and from Sloan (1998) are very similar, except for the value of the parameter $a$ for CO$_2$ (the radius of the impenetrable core), which is almost twice larger in the Sloan’s set of parameters than in Parrish and Prausnitz’s parameters. Additional tests performed by varying the $a$ values in our calculations showed that the relative abundances are in fact very sensitive to this $a$ parameter, as already stated by Papadimitriou et al. (2007). Because more recent sets of Kihara parameters (Jager, 2001; Kang et al., 2001) give a $a$ value for CO$_2$ close

\footnote{Unfortunately, contrary to the data published by Parrish and Prausnitz (1972), these sets do not provide the complete list of Kihara parameters required by the molecules involved in our system.}
to that given by Sloan, the value \( a_{CO_2} \) given by Parrish and Prausnitz (1972) appears rather suspicious. We have thus run again our calculations by using the Kihara set of parameters from Parrish and Prausnitz (1972), in which we have replaced the suspicious \( a_{CO_2} \) value by the one given by Sloan (1998). The corresponding results are given in Fig. 1 which shows that this combined set of parameters (dashed lines) give results which are very similar to those obtained with the whole set of Sloan’s parameters for the Kihara potential. However, because Kihara parameters are only given for a reduced set of species in Sloan (1998), we finally choose to use here the parameters given by Parrish and Prausnitz (1972), but with the \( a_{CO_2} \) value given by Sloan (1998).

### 3 Variability of the methane trapping in clathrate hydrates

The statistical approach presented in the previous section has been used to reinvestigate the work of CC07 and to determine more accurately the composition of clathrate hydrates formed in the near subsurface of Mars as a function of temperature and gas phase composition. In particular, we consider a more plausible composition of the gas phase by taking into account carbon dioxide, nitrogen and argon, namely the most abundant volatiles of the martian atmosphere\(^2\), together with methane in our calculations. Besides, we determine the composition of clathrate hydrates formed at temperatures corresponding to the extreme ones measured in the polar caps (130 K; Kieffer et al., 2001), whereas the work of CC07 was restricted to higher temperatures due to the limitations of the CSMHYD program.

Six different initial abundances of methane in the gas phase have been considered in the present study, namely 0.01%, 0.1%, 1%, 10%, 50% and 90%. The largest values are typical of methane-rich conditions in which CH\(_4\) is supplied from below by microbial or geological processes or from above from ancient atmospheres. In contrast, the lowest values are more typical of recent atmospheric compositions. In each case, we assume that the ratios CO\(_2\)/N\(_2\), CO\(_2\)/Ar, N\(_2\)/Ar are equal to those measured in the present martian atmosphere, and \( x_{CH_4} + x_{Ar} + x_{CO} + x_{N_2} = 1 \).

The evolution with temperature of the relative abundances \( f_G \) (\( G = CH_4, CO_2, N_2, Ar \)) calculated in multiple guest clathrate hydrates corresponding to the various initial abundances of CH\(_4\) considered here is given in Fig. 2. This figure shows that the trapping behavior is the same for each situation, that is the relative abundances of Ar, N\(_2\) and CH\(_4\) slightly increase in clathrate hydrates when the formation temperature increases, whereas that of CO\(_2\) slightly

\(^2\) The present martian atmosphere contains 95% of CO\(_2\), 2.7% of N\(_2\) and 1.6% of Ar (Moroz, 1998).
decreases, irrespective of the initial gas phase abundances. Moreover, Ar and \( N_2 \) are always poorly trapped in clathrate hydrates whereas the incorporation of \( CH_4 \) and \( CO_2 \) strongly depends on the initial composition of the gas phase. Indeed, methane is poorly trapped when its initial abundance in the gas phase is lower than a few percent (see Figs. 2.a to 2.d) and, in such a situation, \( CO_2 \) fills almost entirely the clathrate hydrates with a relative abundance \( f_{CO_2} \approx 1 \). In contrast, when the initial gas phase abundance is enriched in methane, there is a competition between the trapping of \( CO_2 \) and that of \( CH_4 \) which thus have similar abundances in the corresponding clathrate hydrate (Figs. 2.e to 2.f).

Another way for characterizing the trapping in clathrate hydrates is to calculate the abundance ratio for the different gases, which is defined as the ratio between the relative abundance \( f_G \) of a given gas in the multiple guest clathrate hydrate and its initial gas phase abundance \( x_G \) (Thomas et al., 2007, 2008). The abundances ratios calculated for \( CH_4 \), \( CO_2 \), \( Ar \) and \( N_2 \) in the different situations considered here are given in Table 2 together with the corresponding relative abundances in the initial gas phase \( (x_G) \) and in clathrate hydrates \( (f_G) \). Note that we have calculated these abundance ratios at the particular point on the dissociation curves corresponding to the present average atmospheric pressure on Mars, i.e. \( P = 7 \) mbar.

For this particular point, Table 2 shows that the abundance ratio of \( CH_4 \) increases with \( x_{CH_4} \), as a consequence of the larger trapping of methane in the corresponding multiple guest clathrate hydrates (as indicated by the increase of the relative abundance \( f_{CH_4} \)). However, this ratio remains lower than 1 in all situations, indicating that the trapping efficiency of \( CH_4 \) in the multiple guest clathrate hydrates considered here is quite low. On the contrary, the abundance ratio of \( CO_2 \) is always larger than 1, showing the high efficiency of the trapping of \( CO_2 \) in clathrate hydrates. Indeed, even when the gas phase contains less than 10 % of \( CO_2 \), the corresponding multiple guest clathrate hydrate contains about 50 % of \( CO_2 \), as indicated by the values of \( f_{CO_2} \) in Table 2. As a consequence of this preferential trapping of \( CO_2 \) with respect to the other species of the gas phase, the abundance ratio of \( CO_2 \) given in Table 2 increases when the initial gas phase abundance \( x_{CO_2} \) decreases. In other words, although the trapping of \( CH_4 \) is more and more efficient when the initial gas phase is enriched in \( CH_4 \), it remains much less efficient than the trapping of \( CO_2 \). Note that Table 2 also shows that \( Ar \) is slightly better trapped than \( N_2 \). However, the abundances of these two gases are almost negligible in the multiple guest clathrate hydrates considered in the present study.
4 Discussion

Here, we have revisited the work of CC07 devoted to the trapping of CH$_4$ in clathrate hydrates that may exist in the near subsurface of Mars. Our conclusions are similar to those of CC07, although they are based on a more appropriate set of Kihara parameters to describe the interactions between water molecules and guest species. In presence of CO$_2$, a methane-rich clathrate hydrate can be thermodynamically stable only if the gas phase is itself strongly enriched in methane. Hence, CH$_4$-rich clathrate hydrates cannot be formed from the present martian atmosphere, which has been found to be very poor in methane (Mumma et al., 2003; Formisano et al., 2004; Krasnopolsky et al., 2004; Geminale et al., 2008). As a consequence, if they do exist, CH$_4$-rich clathrate hydrates on Mars should have been formed in contact with an early martian atmosphere, much richer in CH$_4$ than the present one. For example, planetary impacts by comets and meteorites in the past could have enriched the martian atmosphere in CH$_4$ (Kress and McKay, 2004). Also, the detection of gray crystalline hematite deposits on Mars could be a proof of an early methane-rich martian atmosphere (Tang et al., 2005). As mentioned in the Introduction of the present paper, another possible origin of CH$_4$-rich clathrate hydrate could be a subsurface source. Indeed, if an internal source of biological (Krasnopolsky et al., 2004) or geological origin (Oze and Sharma, 2005) has existed (or still exists) in the martian subsurface, the present calculations show that stable subsurface CH$_4$-rich clathrate hydrates could form in contact with the produced methane outgassing towards the surface.

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Table 1
Two different sets of parameters for the Kihara potential. $\sigma$ is the Lennard-Jones diameter, $\epsilon$ is the depth of the potential well, and $a$ is the radius of the impenetrable core. These parameters derive from (a) Parrish & Prausnitz (1972), (b) Sloan (1998).

| Ref | Molecule | $\sigma$ (Å) | $\epsilon/k_B$ (K) | $a$ (Å) |
|-----|----------|--------------|--------------------|--------|
| (a) | CH$_4$   | 3.2398       | 153.17             | 0.300  |
|     | N$_2$    | 3.2199       | 127.95             | 0.350  |
|     | CO$_2$   | 2.9681       | 169.09             | 0.360  |
|     | Ar       | 2.9434       | 170.50             | 0.184  |
| (b) | CH$_4$   | 3.1650       | 154.54             | 0.3834 |
|     | N$_2$    | 3.0124       | 125.15             | 0.3526 |
|     | CO$_2$   | 2.9818       | 168.77             | 0.6805 |
|     | Ar       | -            | -                  | -      |
Table 2
Relative abundances of CH$_4$, CO$_2$, Ar and N$_2$ in the initial gas phase ($x_G$) and in clathrates ($f_G$). These ratios are calculated at $P = 7$ mbar, and at the corresponding temperature on the dissociation curves.

| gaz | $x_G$  | $f_G$  | abundance ratio |
|-----|--------|--------|-----------------|
| CH$_4$ | 1×10$^{-4}$ | 1.66×10$^{-5}$ | 0.166 |
|     | 1×10$^{-3}$ | 1.66×10$^{-4}$ | 0.166 |
|     | 1×10$^{-2}$ | 1.67×10$^{-3}$ | 0.167 |
|     | 0.1     | 1.77×10$^{-2}$ | 0.177 |
|     | 0.5     | 0.127    | 0.254 |
|     | 0.9     | 0.496    | 0.551 |
| CO$_2$ | 0.957  | 0.999   | 1.044 |
|     | 0.956  | 0.999   | 1.045 |
|     | 0.947  | 0.998   | 1.054 |
|     | 0.861  | 0.982   | 1.106 |
|     | 0.478  | 0.873   | 1.826 |
|     | 0.096  | 0.504   | 5.250 |
| Ar   | 1.61×10$^{-2}$ | 2.71×10$^{-4}$ | 1.68×10$^{-2}$ |
|     | 1.61×10$^{-2}$ | 2.71×10$^{-4}$ | 1.68×10$^{-2}$ |
|     | 1.59×10$^{-2}$ | 2.69×10$^{-4}$ | 1.69×10$^{-2}$ |
|     | 1.50×10$^{-2}$ | 2.62×10$^{-4}$ | 1.75×10$^{-2}$ |
|     | 0.81×10$^{-2}$ | 1.69×10$^{-4}$ | 2.10×10$^{-2}$ |
|     | 0.16×10$^{-2}$ | 4.56×10$^{-5}$ | 2.83×10$^{-2}$ |
| N$_2$ | 2.72×10$^{-2}$ | 2.20×10$^{-4}$ | 0.81×10$^{-2}$ |
|     | 2.72×10$^{-2}$ | 2.20×10$^{-4}$ | 0.81×10$^{-2}$ |
|     | 2.69×10$^{-2}$ | 2.19×10$^{-4}$ | 0.81×10$^{-2}$ |
|     | 2.40×10$^{-2}$ | 2.05×10$^{-4}$ | 0.85×10$^{-2}$ |
|     | 1.36×10$^{-2}$ | 1.54×10$^{-4}$ | 1.13×10$^{-2}$ |
|     | 0.27×10$^{-2}$ | 5.86×10$^{-5}$ | 2.15×10$^{-2}$ |
Fig. 1. Fraction of CH$_4$ trapped in clathrate hydrates as a function of temperature and of the different CH$_4$/CO$_2$ mixture ratios adopted in the gas phase (see text). The calculations have been performed using either the CSMHYD program proposed by Sloan (1998) (crosses) or the approach proposed in the present paper (solid and dashed lines). The solid lines represent the results obtained with the parameters of the Kihara potential from Sloan (1998). The dashed lines represent the results obtained with the parameters of the Kihara potential from Parrish and Prausnitz (1972) for all species, except for the parameter $a$ for CO$_2$, which comes from Sloan (1998).
Fig. 2. Relative abundances of CO$_2$, CH$_4$, N$_2$ and Ar in clathrate hydrates as a function of temperature for the different methane abundances considered in the present work.