A&A 474, L17–L20 (2007)
DOI: 10.1051/0004-6361:20078072

Astronomy & Astrophysics

LETTER TO THE EDITOR

Clathrate hydrates as a sink of noble gases in Titan's atmosphere

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Received 13 June 2007 / Accepted 11 July 2007

ABSTRACT

We use a statistical thermodynamic approach to determine the composition of clathrate hydrates which may form from a multiple compound gas whose composition is similar to that of Titan's atmosphere. Assuming that noble gases are initially present in this gas phase, we calculate the ratios of xenon, krypton and argon to species trapped in clathrate hydrates. We find that these ratios calculated for xenon and krypton are several orders of magnitude higher than in the coexisting gas at temperature and pressure conditions close to those of Titan's present atmosphere at ground level. Furthermore we show that, by contrast, argon is poorly trapped in these ices. This trapping mechanism implies that the gas-phase is progressively depleted in xenon and krypton when the coexisting clathrate hydrates form whereas the initial abundance of argon remains almost constant. Our results are thus compatible with the deficiency of Titan's atmosphere in xenon and krypton measured by the *Huygens* probe during its descent on January 14, 2005. However, in order to interpret the subsolar abundance of primordial Ar also revealed by *Huygens*, other processes that occurred either during the formation of Titan or during its evolution must be also invoked.

Key words. planet and satellites: individual: Titan – solar system: general

1. Introduction

An unexpected feature of the atmosphere of Titan is that no primordial noble gases other than argon were detected by the Gas Chromatograph Mass Spectrometer (GCMS) aboard the *Huygens* probe during its descent on January 14, 2005. The detected argon includes primordial ^{36}Ar (the main isotope) and the radiogenic isotope ^{40}Ar, which is a decay product of ^{40}K (Niemann et al. 2005). The other primordial noble gases ^{38}Ar, Kr and Xe were not detected by the GCMS instrument, yielding upper limits of 10^{-8} for their mole fractions. In any case, ^{36}Ar/^{14}N is about six orders of magnitude lower than the solar value, indicating that the amount of ^{36}Ar is surprisingly poor within Titan's atmosphere (Niemann et al. 2005).

Several scenarios have been proposed in the literature to interpret the deficiency of Titan's atmosphere in primordial noble gases. The first category of scenarios postulates that this deficiency results from processes that occurred either during Titan's accretion or during the formation of its planetesimals. In this way, Alibert & Mousis (2007) proposed that the building blocks of Titan initially formed at low temperature in the solar nebula and were subsequently partially vaporized in Saturn's subnebula during their migration and accretion, thus leading to the loss of noble gases and of carbon monoxide[1]. Alternatively, Owen (2006) proposed that Titan's planetesimals were directly produced at temperatures high enough in Saturn's subnebula to impede the trapping of the noble gases during their formation and growth. The second category of scenarios postulates that Titan initially incorporated primordial noble gases during its formation but that subsequent processes in its atmosphere or on its surface prevented them from being detected during the descent of the *Huygens* probe. For example, Jacovi et al. (2005) suggested that the aerosols observed in Titan's atmosphere may have cleared its content in noble gases, assuming they were produced from the aggregation of polymers.

Another interpretation is the trapping of atmospheric compounds in clathrate hydrates (Osegovic & Max 2005 – hereafter OM05). Indeed, in such ice structures, water molecules form cages which are stabilized by the trapping of volatiles. Thus, OM05 calculated clathrate hydrate compositions on the surface of Titan by using the program CSMHYD developed by Sloan (1998) and showed that such crystalline ice structures may act as a sink for Xe. However, from these results and because no other noble gases are considered in this program, they assumed similar trapping efficiencies for Ar and Kr. In addition, because the CSMHYD code is not suitable below 160 K for gas mixtures relevant to the atmospheric composition of Titan, OM05 also extrapolated their results to the surface temperature of Titan (about 94 K). Moreover, the stability curves of multiple guest clathrate hydrates calculated from the CSMHYD code strongly depart from the experimental data at low temperature.

Here, we reinvestigate OM05's assumptions and calculate more accurately the trapping of noble gases in clathrate hydrates using a statistical thermodynamic model based on experimental data and on the original work of van der Waals & Platteeuw (1959). In particular, the relative abundances of Xe, Kr, and Ar are explicitly calculated in conditions that are valid for the present temperature and pressure at the surface of Titan. Our results show that, when clathration occurs at low temperature and pressure, the trapping of Xe and Kr is very efficient, contrary to that of Ar. This conclusion is partly consistent with the *Huygens* probe measurements, and supports indirectly the presence of noble gas-rich clathrate hydrates on the surface of Titan.

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[1] CO is several orders of magnitude less abundant than CH_4 in Titan's atmosphere.

2. Clathrate hydrates composition

We follow the method described by Lunine & Stevenson (1985) to calculate the abundance of guests incorporated in clathrate hydrates from a coexisting gas of specified composition. This method uses classical statistical mechanics to relate the macroscopic thermodynamic properties of clathrate hydrates to the molecular structure and interaction energies. It is based on the original ideas of van der Waals & Platteeuw (1959) for clathrate formation, which assume that trapping of guest molecules into cages corresponds to the three-dimensional generalization of ideal localized adsorption. In this model, the occupancy fraction of a guest molecule K for a given type t of cage (t = small or large) in a given type of clathrate hydrate structure (I or II) can be written as

$$y_{K,t} = \frac{C_{K,t}P_K}{1 + \sum_J C_{J,t}P_J}, \tag{1}$$

where the sum at the denominator includes all the species which are present in the initial gas phase. $C_{K,t}$ is the Langmuir constant of species K in the cage of type t, and P_K is the partial pressure of species K. This partial pressure is given by $P_K = x_K \times P$, with x_K the molar fraction of species K in the initial gas phase, and P the total pressure.

The Langmuir constants are determined by integrating the molecular potential within the cavity as

$$C_{K,t} = \frac{4\pi}{k_B T} \int_0^{R_c} \exp\Big(- \frac{w(r)}{k_B T}\Big) r^2 \mathrm{d}r, \tag{2}$$

where R_c represents the radius of the cavity assumed to be spherical, and $w(r)$ is the spherically averaged Kihara potential representing the interactions between the guest molecules and the H_2O molecules forming the surrounding cage. Following McKoy & Sinanoğlu (1963), this potential $w(r)$ can be written for a spherical guest molecule, as

$$\begin{aligned} w(r) &= 2z\epsilon \frac{\sigma^{12}}{R_c^{11} r}\Big(\delta^{10}(r) + \frac{a}{R_c}\delta^{11}(r)\Big) \\ &\quad - \frac{\sigma^6}{R_c^5 r}\Big(\delta^4(r) + \frac{a}{R_c}\delta^5(r)\Big), \end{aligned} \tag{3}$$

with

$$\delta^N(r) = \frac{1}{N}\Big[\Big(1 - \frac{r}{R_c} - \frac{a}{R_c}\Big)^{-N} - \Big(1 + \frac{r}{R_c} - \frac{a}{R_c}\Big)^{-N}\Big]. \tag{4}$$

The Kihara parameters a, σ and ϵ for the molecule-water interactions of the species considered here are given in Table 1. In Eq. (3), z is the coordination number of the cell and r the distance of the guest molecule from the cavity center. These parameters are given in Table 2 and depend on the structure of the clathrate and on the type of the cage (small or large). Note that the Kihara parameters are based on fit to experimental data. However, a systematic study of the influence of their values on the present results would be required to assess the relevance of the present conclusions (Papadimitriou et al. 2006).

Table 1. Parameters of Kihara potential: a is the radius of the impenetrable core, ϵ is the depth of the potential well, and σ is the Lennard-Jones diameter.

Molecule	σ(Å)	a(Å)	ϵ/k_B(K)	Ref.
CH_4	3.1514	0.3834	154.88	(a)
C_2H_6	3.2422	0.5651	189.08	(a)
N_2	3.0224	0.3526	127.67	(a)
Ar	2.829	0.226	155.30	(b)
Kr	3.094	0.307	212.70	(b)
Xe	3.3215	0.2357	192.95	(a)

(a) Jager (2001); (b) Diaz Peña et al. (1982).

Table 2. Parameters for the cavities. b represents the number of small (b_s) or large (b_ℓ) cages per unit cell for a given structure of clathrate, R_c is the radius of the cavity (parameters taken from Sparks et al. 1999), and z the coordination number in a cavity.

Clathrate structure	I		II	
Cavity type	small	large	small	large
b	2	6	16	8
R_c(Å)	3.905	4.326	3.902	4,682
z	20	24	20	28

Finally, the relative abundance f_K of a guest molecule K in a clathrate hydrate can be calculated with respect to the whole set of species considered in the system as

$$f_K = \frac{b_s y_{K,s} + b_\ell y_{K,\ell}}{b_s \sum_J y_{J,s} + b_\ell \sum_J y_{J,\ell}}, \tag{5}$$

where b_s and b_ℓ are the number of small and large cages per unit cell respectively, for the considered clathrate hydrate structure (I or II). The sums in the denominator include all species present in the system. Note that, even if it has been shown that the size of the cages can be reduced by ~10−15% at low temperatures (Shpakov et al. 1998; Besludov et al. 2002), we assume here that this size remains fixed. In the same way, we neglect possible cage distortion due to large guests. Moreover, the relative abundances calculated this way do not discriminate between the various isotopes of the same species.

All calculations have been performed at the dissociation pressure $P = P_{\mathrm{mix}}^{\mathrm{diss}}$ of the multiple guest clathrate hydrate, i.e. temperature and pressure conditions at which the clathrate hydrate is formed. This dissociation pressure can be deduced from the dissociation pressure P_K^{diss} of a pure clathrate hydrate of species K, as (Hand et al. 2006)

$$P_{\mathrm{mix}}^{\mathrm{diss}} = \Bigg(\sum_J \frac{x_J}{P_J^{\mathrm{diss}}}\Bigg)^{-1}. \tag{6}$$

The dissociation pressures P_J^{diss} derived from laboratory measurements follow an Arrhenius law (Miller 1961) as

$$\log(P^{\mathrm{diss}}) = A + \frac{B}{T}, \tag{7}$$

where P^{diss} is expressed in Pa and T is the temperature in K. The constants A and B fit to experimental data (Lunine & Stevenson 1985; Sloan 1998) in the present study are given in Table 3. Note that, in the present approach, the dissociation pressures and the Langmuir constants are independently calculated.

3. Results and discussion

We determine the relative abundances f_{Xe}, f_{Kr} and f_{Ar} with respect to all guests incorporated in clathrate hydrate formed from a gas whose composition is similar to that of Titan's atmosphere. Similarly to OM05, we assume that N_2, CH_4, C_2H_6 and the considered noble gas (Xe, Kr or Ar) are the main atmospheric compounds of the initial gas phase (see Table 4). Note that when

Table 3. Parameters of the dissociation curves for various single guest clathrate hydrates. A is dimensionless and B is in K.

Molecule	*A*	*B*
CH_4	9.89	−951.27
C_2H_6	10.65	−1357.42
N_2	9.86	−728.58
Ar	9.34	−648.79
Kr	9.03	−793.72
Xe	9.55	−1208.03

Table 4. Initial gas phase abundances considered in the atmosphere of Titan. For each noble gas (Xe, Kr and Ar), three different compositions of the initial gas phase are investigated.

Molecule	Molar fractions (%)		
Noble gas	0.1	0.055	0.01
CH_4	4.8	4.845	4.89
N_2	95	95	95
C_2H_6	0.1	0.1	0.1

the calculations are performed for one noble gas (Xe, Kr or Ar), the two others are excluded from the initial gas composition. The gas phase abundance of N_2 is taken similar to OM05 and that of CH_4 has been updated from the *Huygens* measurements (Niemann et al. 2005). The atmospheric abundance of ethane has been fixed to 0.1% in our calculations. For each considered noble gas, three initial abundances have been selected in order to investigate the influence of its initial concentration in the gas phase, on the clathrate hydrate's trapping efficiency. The abundance of CH_4 is then varied in consequence to preserve the global volatile budget. Moreover, we have calculated the relative abundances of noble gases for both clathrate hydrates structures I and II. Because the conclusions of our calculations are similar for both structures, we focus here on the results obtained for structure I only. Note that this structure corresponds to that derived by OM05 from the CSMHYD program.

Figures 1 to 3 represent the evolution of $f_{\rm Xe}$, $f_{\rm Kr}$ and $f_{\rm Ar}$ respectively, in a multiple guest clathrate hydrate as a function of T along the dissociation curve $P^{\rm diss}_{\rm mix} = f(T)$, and for three different noble gas abundances in the initial gas phase (see Table 4). Figure 1 shows that, irrespective of the initial gas phase abundance of Xe, its relative abundance progressively increases in clathrate hydrate when T, and hence $P^{\rm diss}_{\rm mix}$, decrease. This behavior of the Xe clathration efficiency agrees with the calculations of OM05 (e.g. their Fig. 5). Similar behavior is seen with Kr, as shown in Fig. 2. By contrast, the relative abundance of Ar in clathrate hydrate decreases when T and $P^{\rm diss}_{\rm mix}$ decrease, as shown in Fig. 3. This figure also shows that $f_{\rm Ar}$ gradually converges towards zero at temperatures below ∼100 K, irrespective of its initial concentration in the gas phase. This huge difference between the trapping of Ar, Xe and Kr in clathrate hydrate is mostly due to the higher values of the Kihara parameters of the two latter molecules (see Table 1) which are responsible for a stronger interaction energy with the surrounding water molecules in clathrate hydrate cages.

In addition to the relative abundances f_K discussed above, we have also calculated the abundance ratio for the three considered noble gases Xe, Kr and Ar (Table 5). This ratio is defined as the ratio between the relative abundance f_K of a given noble gas in the multiple guest clathrate hydrate and its initial gas phase abundance x_K (see Table 4). We considered one particular point located on the dissociation curve of the multiple guest clathrate hydrate under study in our calculations. This point corresponds to the present atmospheric pressure at the ground level of Titan ($P^{\rm diss}_{\rm mix}$ = 1.5 bar) and to a temperature value of 171 K, as indicated by the clathrate hydrate dissociation curve. Table 5 shows that, depending on the initial gas phase conditions and for this particular point, the relative abundances of Xe and Kr trapped in clathrate hydrates are between 168 and 555 times those in the initial gas phase. Considering the current amount of atmospheric

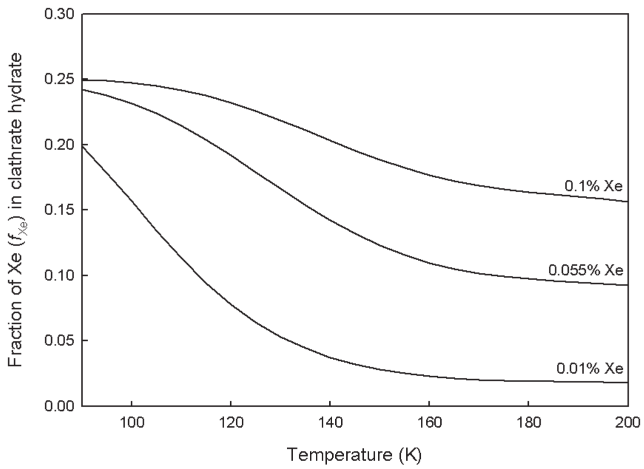

Fig. 1. $f_{\rm Xe}$ in a multiple guest clathrate hydrate, as a function of temperature and of the initial gas phase composition (see Table 4).

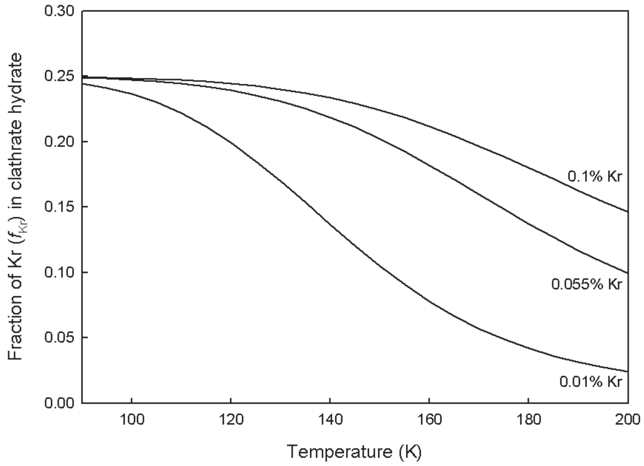

Fig. 2. Same as Fig. 1 but for Kr.

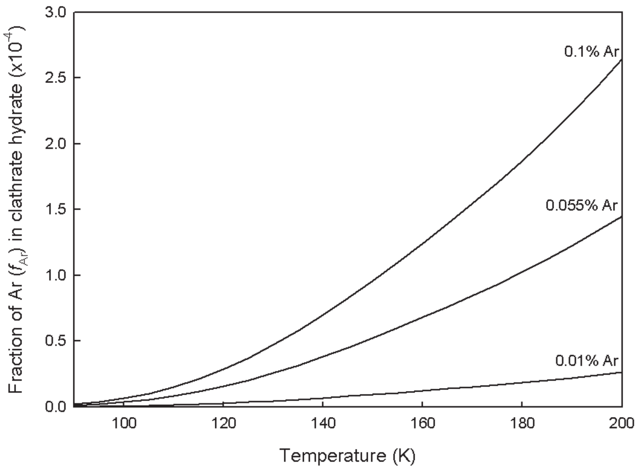

Fig. 3. Same as Fig. 1 but for Ar.

Table 5. Abundance ratios of noble gas in clathrate hydrate to noble gas in the initial gas phase for Xe, Kr and Ar. These ratios are calculated at T = 171 K and $P_{\mathrm{mix}}^{\mathrm{diss}}$ = 1.5 bar.

Initial molar fraction in gas	abundance ratio
Xe gas	
0.001	168
0.00055	184
0.0001	204
Kr gas	
0.001	195
0.00055	285
0.0001	555
Ar gas	
0.001	1.577×10^{-1}
0.00055	1.572×10^{-1}
0.0001	1.566×10^{-1}

CH_4 calculated by Lunine & Tittemore (1993) ($\sim 3 \times 10^{20}$ g), we have calculated that a 0.1% gas phase abundance of a given noble gas translates into the presence of $\sim 3.9 \times 10^{17}$ moles in Titan's atmosphere. Assuming full efficiency for the sink mechanism described here, the amount of water needed for the trapping of Xe or Kr in clathrate hydrates at the surface of the satellite is $\sim 4 \times 10^{19}$ g. This roughly corresponds to a single guest (Xe or Kr) clathrate hydrate layer ~50 cm thick at the surface of Titan.

Such an efficient trapping may be high enough to significantly decrease the atmospheric concentrations of Xe and Kr, provided that clathrate hydrates are abundant enough on the surface of Titan. On the contrary, with an abundance ratio much lower than 1, Ar is poorly trapped in clathrate hydrate and the Ar atmospheric abundance consequently remains almost constant.

4. Conclusions

The trapping mechanism we investigated can explain the deficiency in primordial Xe and Kr observed by *Huygens* in Titan's atmosphere. Indeed, our results show that these noble gases could have been progressively absorbed in clathrate hydrates located at the surface of Titan during its thermal history. By contrast, our results show that the trapping of Ar is poor in clathrate hydrates. As a consequence, such a mechanism alone cannot interpret the subsolar abundance of primordial Ar which is also observed in Titan's atmosphere. The different scenarios invoked in the Introduction may thus have worked together with the trapping in clathrate hydrates to explain the deficiency in primordial Xe, Kr and Ar. Note that boulders observed in images from *Huygens* have been invoked as evidence for the existence of clathrate hydrates on the surface of Titan (OM05). However, further *in situ* measurements are required to investigate whether noble gases-rich clathrate hydrates really exist on the surface of Titan.

Acknowledgements. We acknowledge E. Dendy Sloan and Nicolas Iro for fruitful discussions and information on their work. We also acknowledge Gabriel Tobie for useful comments on this manuscript.

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