# Equilibrium Pressure of Ethane, Acetylene, and Krypton Clathrate Hydrates below the Freezing Point of Water

**6 AUTHORS**, INCLUDING:

Ulysse Marboeuf
Universität Bern

**47** PUBLICATIONS **330** CITATIONS

Bernard Schmitt
University Joseph Fourier - Grenoble 1

**380** PUBLICATIONS **5,773** CITATIONS

# Equilibrium Pressure of Ethane, Acetylene, and Krypton Clathrate Hydrates below the Freezing Point of Water

Ulysse Marboeuf,[*,†] Nicolas Fray,[‡] Olivier Brissaud,[†] Bernard Schmitt,[†] Dominique Bockelée-Morvan,[§] and Daniel Gautier[§]

[†]UJF-Grenoble 1/CNRS-INSU, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), UMR 5274, 38041 Grenoble, France

[‡]LISA, Laboratoire Interuniversitaire des Systèmes Atmosphériques, UMR CNRS 7583, Université Paris-Est Créteil (UPEC) et Université Paris Diderot (UPD), Créteil, France

[§]LESIA, CNRS UMR 8109, UPMC, Université Paris-Diderot, Observatoire de Paris, 5 pl. Jules Janssen, 92195 Meudon, France

**ABSTRACT:** We report measurements of the equilibrium pressure of single guest clathrate hydrates of $C_2H_6$, $C_2H_2$, and Kr at low temperatures (mainly in the range (150 to 230) K). The results are compared with other data reported in the literature and used to determine new empirical *correlation* laws allowing to calculate the equilibrium pressure of clathrates of these species at any temperature below the freezing point of water. Enthalpies of clathrate formation/dissociation for these molecules are estimated using the Clausius–Clapeyron equation and show good agreement with previous reported calorimetric measurements. These results are of particular interest for studies of extraterrestrial ice-rich environments such as comets and icy moons in the solar system.
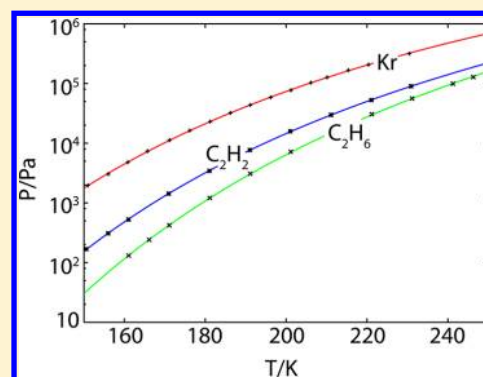
## INTRODUCTION

Clathrate hydrates or *gas hydrates* (hereafter clathrates) are crystalline solids composed of water and gas. The lattice of water molecules is organized in the form of cages which are stabilized by the inclusion of gas molecules. This structure of water ice selectively retains and releases the gases trapped in cages and is of particular interest to explain the deficiency/enrichment of some molecular species in some astrophysical environments. For example, the presence of clathrates in comets[1−9] and icy moons of giant planets[10] has been discussed for a long time. Models of ice formation in the protoplanetary disk[11−18] show that icy bodies formed during the cooling of the solar nebula could be partially made up of clathrates. Several authors invoked the presence of clathrates to explain the anomalous relative abundances measured in solar system bodies.[14,15,19]

Characterizing $C_2H_6$, $C_2H_2$, and Kr clathrates is of particular interest for studying extraterrestrial environments. $C_2H_6$ and $C_2H_2$ have been detected in the gas phase of comets[20] and could be partially trapped in clathrates within these objects together with the main cometary volatile molecules.[9] Moreover, $C_2H_6$ could have been sequestered by clathrates in the cryovolcanic subsurface of Titan, the largest satellite of Saturn,[10] thus explaining its deficiency in this moon. Kr, as other noble gases, has never been detected in cometary environments because its remote observation is very difficult.[20] However, its incorporation in cometary nuclei is suspected: noble gases of Earth could come partially from these objects,[21] and models of ice formation in protoplanetary disks show that this element could have been partially trapped in clathrates within icy bodies.[17]

In this paper, we report measurements of the equilibrium pressure of single guest clathrates of $C_2H_6$, $C_2H_2$, and Kr below the freezing point of water at temperatures relevant for extraterrestrial environments. The results are compared with other data reported in the literature and are used to determine new empirical correlation laws allowing to calculate the equilibrium pressure of these single guest clathrates at any temperature below the freezing point of water. These new empirical laws are then compared to laws currently used in astrophysical papers. Enthalpies of clathrate dissociation are also estimated using the Clausius–Clapeyron equation. The values derived in this work are in good agreement with previous published calorimetric measurements.

## EXPERIMENTAL METHOD

**Experimental System.** Figure 1 shows the schematic diagram of the apparatus used in this study. This experimental system has already been described in a previous paper,[22] and we provide only a brief description in this section. The equilibrium pressure of clathrates is measured in a cylindrical copper reactor of about 13 cm$^3$ inner volume. This reactor is composed of two
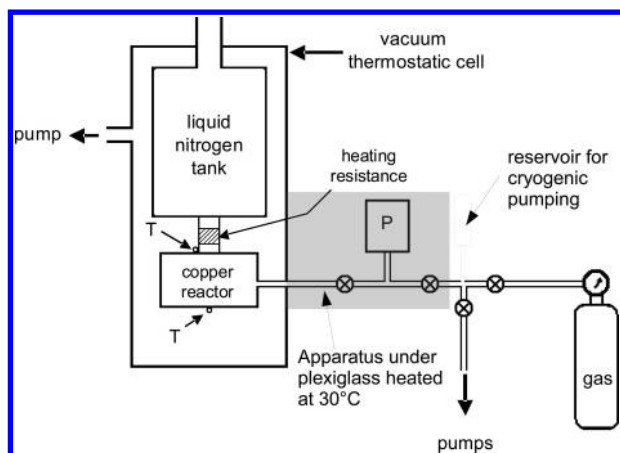
**Figure 1.** Schematic view of the experimental system used to measure the equilibrium pressure of single guest clathrates of $C_2H_6$, $C_2H_2$, and Kr.

parts connected by an indium gasket which ensures its sealing at low temperatures. It is located inside a thermostatic cell (ABT SORIME), evacuated to about $10^{-3}$ Pa using a diffusion pump (Alcatel) backed by a diaphragm pump, and connected to a liquid nitrogen dewar via a copper finger. A heating resistance is fixed on the upper copper finger, and two temperature sensors (silicon diodes) are glued on the lower and upper parts of the reactor. Resistance and temperature sensors are all connected to a temperature controller (model 331 of Lakeshore), which ensures a temperature stability of about ± 0.03 K. Finally, the apparatus allows us to measure temperatures from (77 to 300) K, with an uncertainty of about 0.01 K.

The reactor is evacuated using a turbo-molecular pump (TMU-071P, Pfeiffer) backed by a dry scroll vacuum pump (XDS 5, Edwards). The pressure is measured in the line located between the reactor and the pumping group using either (1) an absolute metal membrane pressure sensor (Baratron 690-A13T-RB, MKS) allowing us to measure the pressure between $(1.33 \cdot 10^2$ and $1.33 \cdot 10^5)$ Pa with an accuracy 0.08 % of the reading value, or (2) a bonded strain gauge absolute pressure transducer (Teledyne Taber, model 2201) allowing us to measure pressures between $(0$ and $13.8 \cdot 10^5)$ Pa with a measurement uncertainty of $\pm$ $10^2$ Pa. Temperature and pressure are recorded as a function of time with a resolution of a few seconds using a laboratory-made software. Note that the reactor includes neither a stirrer nor a shaker. To avoid fluctuations of temperature (and hence pressure) induced by daily room temperature changes, we placed the apparatus (pressure sensors and tubing) under Plexiglas maintained at a regulated temperature of 30 °C.

**Materials.** Table 1 reports the purities and suppliers of the chemical species used in this work. $C_2H_2$ gas is mixed with $N_2$, which represents a volume fraction of 0.4 % of the total gas phase. To improve the purity of this gas before its injection into the reactor, we added a cooled reservoir between the entry of

**Table 1. Purities and Suppliers of Gas**

| chemical species | purity (molar fraction) | supplier |
|---|---|---|
| Xe | 99.998 % | Air Liquide |
| Kr | 99.998 % | Air Liquide |
| $C_2H_6$ | 99.95 % | Air Liquide |
| $C_2H_2$ | 99.6 % | Air Liquide |

the reactor and the gas cylinder to eliminate $N_2$ (see Figure 1). The fractionation of the two gases is obtained by cryogenic pumping: the reservoir is immersed in liquid nitrogen at 77 K; then an amount of $C_2H_2$ gas from the bottle is introduced and condenses in the reservoir; by pumping the residual gas phase ($N_2$ essentially), only $C_2H_2$ remains in solid state in the reservoir. At least 99 % of $N_2$ impurity is eliminated in this operation. This step is controlled by measuring the initial and residual pressures with the first pressure sensor (Baratron). The reservoir is then heated at room temperature, then cooled and pumped again. This operation is repeated at least three times to ensure the removal of almost all of the initial $N_2$ in the gas phase. The final $N_2$ impurity level is then lower than 1 %. The water used to form clathrates in the experiments has been purchased from Merck and is produced for online analysis.

**Procedure.** The procedure used to form the clathrate structure is described in Fray et al. (2010),[22] and we briefly summarize the method in this section. We form single guest clathrates of Xe in a first reactor in which we introduce about 5 cm$^3$ of liquid water and about 200 kPa of Xe. This reactor is then immersed in a water bath at 1 °C during a few minutes, and we obtain about 1 g of clathrates of Xe. The sample is then transferred in the second reactor (copper reactor), in a cold room at about −20 °C, and the experimental system is assembled as in Figure 1. Air is then pumped.

To study the equilibrium pressure of clathrates of single guest species $C_2H_6$, $C_2H_2$, and Kr, we have to convert the initial sample of Xe to $C_2H_6$, $C_2H_2$, or Kr clathrates. For this, the reactor is maintained at a constant temperature of 220 K. The gaseous Xe is then evacuated by pumping the clathrate sample, leading to its partial decomposition, until gaseous Xe stops being released by the sample. In a second step, we inject in the reactor an amount of gas to a pressure larger than the expected equilibrium pressure of the desired species ($C_2H_6$, $C_2H_2$, or Kr). This pressure can reach several times the estimated (extrapolated) equilibrium pressure of the single species clathrate but is always lower than the corresponding vapor pressure of the pure species solid phase. The formation of the single guest clathrate results in a rapid decrease of the pressure in the isolated reactor. After pressure stabilization, the whole operation (decomposition/formation of clathrate) is repeated at least 10 times to ensure the removal of almost all of the initial Xe in the clathrate structure.

At this time of the procedure, we assume that we have obtained a sample of pure clathrate of the desired species. Some small Xe clathrate residues can remain deeply embedded in ice grains of the sample, but they do not interact with the gas phase. The temperature of the reactor is then maintained constant, and we reduce the pressure below the theoretical or experimental equilibrium pressure known in the literature. A pressure increase is then observed, as shown in Figure 2, due to the decomposition of clathrates and the release of gas molecules in the closed reactor. Once the pressure is stabilized, we obtain a first (under-)estimate of the clathrate equilibrium pressure from the partial decomposition of the clathrate structure. Then, we inject an overpressure of gas in the reactor and a pressure decrease is observed due to the formation of clathrates and encapsulation of the gas molecules. We obtain the second (over)estimate of the clathrate equilibrium pressure from reformation of the clathrate structure. This procedure is repeated several times at the same temperature until convergence of both pressures toward a common equilibrium pressure is achieved with a low relative error (as much as

3409

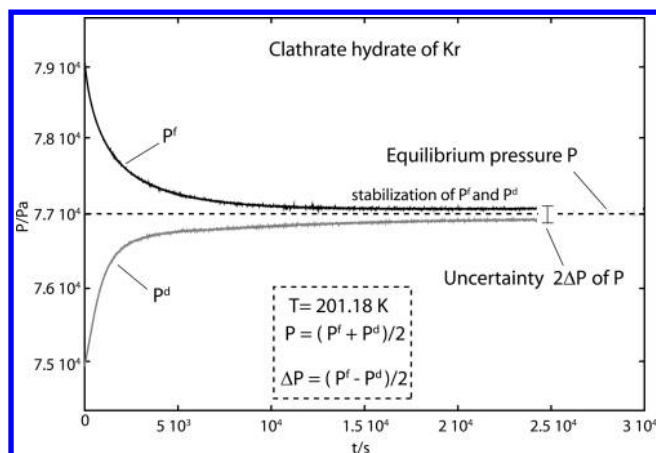dx.doi.org/10.1021/je3004595 | *J. Chem. Eng. Data* 2012, 57, 3408–3415

**Figure 2.** Procedure to obtain the clathrate equilibrium pressure $P$ at temperature $T$. $P$ is obtained by the arithmetic average of the two closest values of decomposition $P^d$ and formation $P^f$ pressures, while the total uncertainty is the difference between these two values divided by 2.

**Table 2. Parameters[a] Describing the Equilibrium Pressure of Clathrates as a Function of the Temperature Using Equation 1**

| chemical species | $A$ | $B$ | $T/K$ |
|---|---|---|---|
| Kr | 22.3934 | −2237.82 | 151 to 230 |
| $C_2H_6$ | 24.8246 | −3211.75 | 161 to 246 |
| $C_2H_2$ | 23.20757 | −2725.19 | 151 to 231 |

[a]$A$ and $B$ are the parameters of the empirical relation. $A$ is dimensionless, and $B$ is in kelvin.

$$\frac{d\ln(P)}{d(1/T)} = -\frac{H_P^{cl}}{R} \tag{2}$$

where $R$ is the gas constant.

The values for the three species $C_2H_6$, $C_2H_2$, and Kr and their corresponding calorimetric measurements from Handa (1986)[31−40] are given in Table 3.

**Table 3. Enthalpy of Clathrate Dissociation $H^{cl}$ from Clausius−Clapeyron Equation 2 and Calorimetric Measurements**

| chemical species | $H_P^{cl\,a}$ | $H^{cl,o\,b}$ |
|---|---|---|
| | kJ·mol$^{-1}$ | kJ·mol$^{-1}$ |
| Kr | 18.6 | 19.54 ± 0.24[31] |
| $C_2H_6$ | 26.7 | 25.7 ± 0.24[40] |
| $C_2H_2$ | 22.66 | no published data |

[a]Enthalpy determined by Clausius−Clapeyron. [b]Enthalpy determined by calorimetric measurement.

possible $\Delta P \leq 3$ %). The equilibrium pressure $P$ is then supposed to be the arithmetic average of the two closest values of decomposition $P^d$ and formation $P^f$ pressures, while the maximum total uncertainty is supposed to be the difference $\Delta P$ between these two values (see Figure 2). This uncertainty is mostly determined by the kinetics of clathrate formation/decomposition that depends on temperature, the difference between the gas pressure and the equilibrium pressure of the clathrate, the availability of water molecules to form the cage structure, and on a number of uncontrolled parameters that can lead to the metastability of clathrates.[8,23−28] The equilibrium can be fast ($\leq 1$ day) at temperatures higher than 190 K. However at lower temperatures, several days are need to reach and measure the equilibrium pressure within a few percents. For all clathrate hydrates of the desired species ($C_2H_6$, $C_2H_2$, or Kr), both the formation and dissociation processes are made at a fixed temperature on the same sample of clathrate hydrate. The uncertainty on the temperature is then about ± 0.02 K.

### ■ RESULTS AND DISCUSSION

All experimental equilibrium data of single guest clathrates measured in this work, as well as the ones already published in the literature for species Kr, $C_2H_6$ and $C_2H_2$ are reported in Tables 4, 5, and 6 and are plotted in Figures 3, 5, and 7, respectively. The figures also display our empirical correlation laws and the deviation of the experimental data from these empirical laws.

Empirical correlation laws are determined by fitting our data with the following empirical relation:

$$\ln(P) = A + \frac{B}{T} \tag{1}$$

in which $P$ and $T$ are the pressure (in Pa) and the temperature (K). The parameters $A$ and $B$ for the three species $C_2H_6$, $C_2H_2$, and Kr are given in Table 2. These empirical correlation laws can be used at any temperature below the freezing point of water.

To assess the reliability of our data, we estimated the enthalpy of clathrate dissociation $H_P^{cl}$ using the Clausius−Clapeyron equation given by the relation:

These values are of particular interest to calculate the energy of phase change between water ice and clathrate in models of cometary nuclei[41] during their physicochemical evolution around the sun as well as for others applications to astrophysical models.

**Clathrate of Krypton, Kr.** We performed 16 measurements, ranging from (151 to 230.5) K, given in Table 4 and Figure 3. These data partially overlap and extend the temperature range of the experimental data of Jin et al. (2011)[29] and fully overlap those of Barrer and Edge (1967).[30] These latter values show a progressive deviation, from about 25 % at 202.9 K to about 300 % at 149 K, from our data and the ones of Jin et al. (2011).[29] One can note that a similar deviation from the data of Barrer and Edge (1967)[30] has already been observed for Xe clathrates (see Fray et al., 2010[22]).

Moreover, the data of Jin et al. (2011)[29] show a systematic positive deviation between 6 % and 8 % from our measurements. In summary, the three data sets that currently exist in the literature on the clathrate equilibrium pressure of Kr do not overlap and hence do not converge in a common relationship. So, although the data sets of other authors are not necessarily in error, we have taken into account only our measurements for the determination of the empirical relation of the equilibrium pressure of the single guest clathrate of Kr (see Table 2). It reproduces our nominal experimental measurements with a relative deviation of less than 2.5 % (without error bins, see Figure 3, upper panel).

From the slope of this $P(T)$ curve, $H_P^{cl}$ is estimated to about 18.6 kJ·mol$^{-1}$ in the temperature range (151 to 230) K. This value is in agreement with the one (18.5 kJ·mol$^{-1}$) obtained by Jin et al. (2011)[29] in the temperature range (204 to 270) K and the value $H^{cl,o}$ of 19.54 ± 0.24 kJ·mol$^{-1}$ obtained at 273 K from

3410

dx.doi.org/10.1021/je3004595 | J. Chem. Eng. Data 2012, 57, 3408−3415

**Table 4. Experimental Data for the Equilibrium of Single Guest Clathrate of Kr below the Freezing Point of Water**

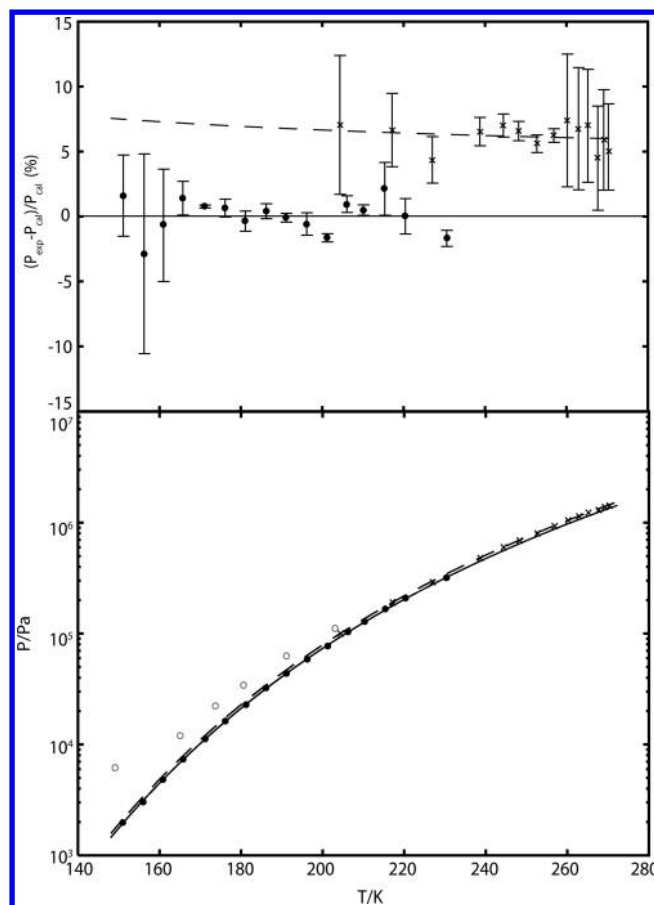| $T/K$ | $\Delta T/K$ | $P/Pa$ | $\Delta P/Pa$ | $\Delta P/P$ (%) | reference |
|---|---|---|---|---|---|
| 202.9 | 0.1 | 111191 | unknown | unknown | 30 |
| 191.0 | 0.1 | 62528 | unknown | unknown | 30 |
| 180.6 | 0.1 | 34264 | unknown | unknown | 30 |
| 173.7 | 0.1 | 22265 | unknown | unknown | 30 |
| 164.9 | 0.1 | 12012 | unknown | unknown | 30 |
| 149.0 | 1.0 | 6266 | unknown | unknown | 30 |
| 270.4 | 0.2 | 1420000 | 50000 | 3.52 | 29 |
| 269.2 | 0.2 | 1380000 | 50000 | 3.62 | 29 |
| 267.7 | 0.2 | 1300000 | 50000 | 3.85 | 29 |
| 265.2 | 0.2 | 1230000 | 50000 | 4.06 | 29 |
| 262.9 | 0.2 | 1140000 | 50000 | 4.39 | 29 |
| 260.2 | 0.2 | 1050000 | 50000 | 4.76 | 29 |
| 256.9 | 0.2 | 930000 | 5000 | 0.54 | 29 |
| 252.7 | 0.2 | 800000 | 5000 | 0.63 | 29 |
| 248.3 | 0.2 | 690000 | 5000 | 0.73 | 29 |
| 244.4 | 0.2 | 600000 | 5000 | 0.83 | 29 |
| 238.7 | 0.2 | 480000 | 5000 | 1.04 | 29 |
| 227.0 | 0.2 | 290000 | 5000 | 1.72 | 29 |
| 217.2 | 0.2 | 190000 | 5000 | 2.63 | 29 |
| 204.4 | 0.2 | 100000 | 5000 | 5 | 29 |
| 230.45 | 0.02 | 316535 | 1972 | 0.62 | this work |
| 220.38 | 0.02 | 206734 | 2802 | 1.36 | this work |
| 215.39 | 0.02 | 166777 | 3321 | 1.99 | this work |
| 210.14 | 0.02 | 126642 | 532 | 0.42 | this work |
| 206.12 | 0.02 | 103279 | 658 | 0.64 | this work |
| 201.18 | 0.02 | 77130 | 272 | 0.35 | this work |
| 196.19 | 0.02 | 58749 | 506 | 0.86 | this work |
| 191.14 | 0.02 | 43681 | 157 | 0.36 | this work |
| 186.22 | 0.02 | 32192 | 190 | 0.59 | this work |
| 181.22 | 0.02 | 22952 | 176 | 0.76 | this work |
| 176.19 | 0.02 | 16296 | 114 | 0.7 | this work |
| 171.17 | 0.02 | 11242 | 5 | 0.05 | this work |
| 165.73 | 0.02 | 7366 | 94 | 1.28 | this work |
| 160.86 | 0.02 | 4789 | 209 | 4.37 | this work |
| 156 | 0.02 | 3039 | 240 | 7.9 | this work |
| 150.98 | 0.02 | 1970 | 60 | 3.07 | this work |



**Figure 3.** Equilibrium pressure of single guest clathrate of Kr (lower panel) and deviations of experimental data from our empirical relation (upper panel) as a function of the temperature: ●, this work; ×, Jin et al. (2011);[29] O, Barrer and Edge (1967);[30] solid black line, our empirical relation; dashed black line, empirical relation from Jin et al. (2011).[29]

earlier calorimetric measurements.[31] Considering this calorimetric value as the reference at 273 K for the enthalpy of dissociation of Kr clathrate, this leads to a relative difference/error of about 5 % relative to our value.

For a better accuracy, it is interesting to investigate the variation of the clathrate dissociation enthalpy $H^{cl}(T)$ with temperature to compare values published in the same temperature range as our data. $H^{cl}(T)$ varies following the relation:[32]

$$H^{cl}(T) = H^{cl,o} + \int_{T_0}^{T} \Delta C_x^{cl}(T) dT \qquad (3)$$

$\Delta C_x^{cl}(T)$ is the heat capacity difference between water ice and the clathrate structure of the species $x$ ($x$ = Kr here) at temperature $T$:

$$\Delta C_x^{cl}(T) = n_{hyd} C_{H_2O}^{i} + C_{p,x}^{g} - C_x^{cl} \qquad (4)$$

where $C_x^{cl}$ and $C_{H_2O}^{i}$ are the heat capacities of the clathrate of gas $x$ and of pure water ice, respectively, and $C_{p,x}^{g}$ is the heat capacity of the gas $x$. Taking into account the values of the heat capacity of Kr clathrate measured by Handa (1986)[31] from (85

to 270) K, and assuming a heat capacity $C_{p,x}^{g}$ of the noble gas of $5/2R$, we obtain a clathrate dissociation enthalpy $H^{cl}(T)$ varying from (19 to 19.3) kJ·mol$^{-1}$. These values lead to a relative variation $(H_P^{cl} - H^{cl}(T))/H^{cl}(T)$ from (2 to 4) % between (151 and 230) K, the temperature range of our data (see Figure 4). So, our constant enthalpy of Kr clathrate dissociation obtained from the Clausius–Clapeyron eq 2 is in good agreement with the values determined by calorimetric analysis.

**Clathrate of Ethane, $C_2H_6$.** We performed 11 measurements ranging from (161.1 to 246.3) K which are given in Table 5 and Figure 5. There are five other papers providing experimental data of equilibrium pressure of $C_2H_6$ clathrate. Our data fully cover the range of temperatures of Falabella and Vanpee (1974)[33] data and extend all of the previous published data at lower temperatures. The data of Falabella and Vanpee (1974)[33] (temperature range from (200 to 240) K) and Roberts et al. (1940)[34] (260 to 270 K) show systematic positive deviations up to 23 % compared to the empirical relation derived from our values only. However, our data fit fairly well those of Deaton and Frost (1946),[35] Yasuda and Ohmura (2008),[36] and Mohammadi and Richon (2010).[37] We have then taken into account only these data together with our measurements for the determination of the empirical relation of the equilibrium pressure of the single guest clathrate of $C_2H_6$
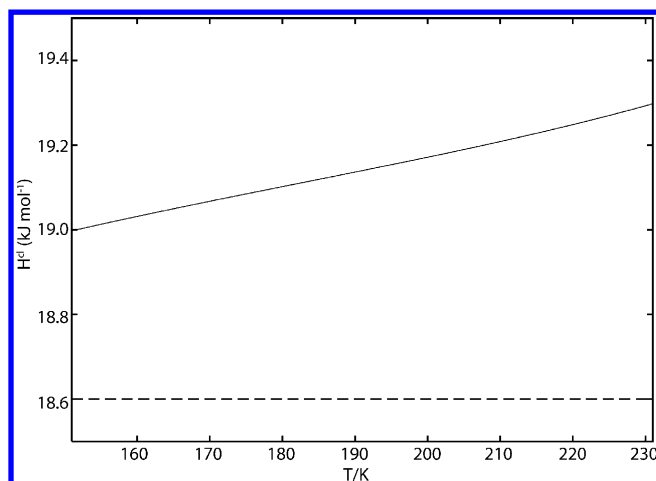
**Figure 4.** Enthalpy of clathrate dissociation of Kr as a function of temperature in the temperature range (151 to 230) K of our data: dashed black line, our value; black line, relation from Handa (1986).[31] Our value is obtained from the $P(T)$ slope of our data and by using eq 3.

(see Table 2). This relation reproduces the measurements with a relative deviation of ± 2.5 % (see Figure 5, upper panel). The expression of Miller (1961),[39] an interpolation of unpublished experimental measurements performed from (161 to 243) K, shows a progressive deviation from our relation with a maximum of about 8 % at 160 K.

From the slope of this empirical law, $H_P^{cl}$ is approximately 26.7 kJ·mol$^{-1}$ in the temperature range (161 to 246.3) K. Our value is in very good agreement with the one (26.4 kJ·mol$^{-1}$) obtained from the slope of Miller (1961)[39] in the temperature range (161 to 243) K and the value $H^{cl,o}$ (25.7 ± 0.24 kJ·mol$^{-1}$) obtained at 273 K from calorimetric measurements.[40] Taking into account the calorimetric value $H^{cl,o}$ as the reference at 273 K for the enthalpy of clathrate dissociation of C$_2$H$_6$, this leads to a relative difference value of about 3.9 %.

We can now investigate the variation of clathrate dissociation enthalpy with temperature using eq 3. By taking into account values of the heat capacity of clathrate $C_x^{cl}$ measured by Handa (1986)[40] from (85 to 270) K, and assuming the heat capacity of the gas $C_{p,x}^{g}$ given by Chao et al. (1973),[42] we obtain a clathrate dissociation enthalpy $H^{cl}(T)$ varying from (26.9 to 26.0) kJ·mol$^{-1}$. These values lead to a relative variation ($H_P^{cl}$ − $H^{cl}(T))/H^{cl}(T)$ from (−0.6 to 2.7) % between (161 and 246) K, the temperature range of our data set (see Figure 6). Our calculation of a constant enthalpy of clathrate dissociation of C$_2$H$_6$ using the Clausius−Clapeyron equation is then in good agreement with the calorimetric analysis.

**Clathrate of Acetylene, C$_2$H$_2$.** We performed 10 measurements ranging from (150.5 to 231) K given in Table 6 and Figure 7. To our knowledge only Stackelberg and Müller (1954)[38] published two experimental data of equilibrium pressure of acetylene clathrate, but the value at 257.75 K shows a very large deviation of about a factor of 3 compared to our values. On the other hand, Miller (1961)[39] published an equilibrium pressure empirical law based on unpublished experimental data performed from (158 to 231) K that confirms this deviation. We have then taken into account only our data for the determination of the empirical relation of the equilibrium pressure of the single guest clathrate of C$_2$H$_2$ (see Table 2). It reproduces our experimental measurements with a relative deviation of ± 2 % (see Figure 7, upper panel). The

**Table 5. Experimental Data for the Equilibrium Pressure of Single Guest Clathrate of C$_2$H$_6$**

| $T$/K | $\Delta T$/K | $P$/Pa | $\Delta P$/Pa | $\Delta P/P$ (%) | reference |
|---|---|---|---|---|---|
| 269.3 | unknown | 441000 | unknown | unknown | 34 |
| 260.9 | unknown | 290000 | unknown | unknown | 34 |
| 260.8 | unknown | 294000 | unknown | unknown | 34 |
| 272.0 | unknown | 457000 | unknown | unknown | 35 |
| 269.3 | unknown | 405000 | unknown | unknown | 35 |
| 266.5 | unknown | 357000 | unknown | unknown | 35 |
| 263.6 | unknown | 313000 | unknown | unknown | 35 |
| 240.8 | 0.1 | 101300 | 666 | 0.7 | 33 |
| 240.4 | 0.1 | 98100 | 666 | 0.7 | 33 |
| 230.2 | 0.1 | 56400 | 666 | 1.2 | 33 |
| 215.7 | 0.1 | 22100 | 666 | 3 | 33 |
| 200.8 | 0.1 | 8300 | 666 | 8 | 33 |
| 271.9 | 0.1 | 443000 | 3000 | 0.7 | 36 |
| 269.7 | 0.1 | 403000 | 3000 | 0.7 | 36 |
| 267.3 | 0.1 | 360000 | 3000 | 0.8 | 36 |
| 264.3 | 0.1 | 315000 | 3000 | 1 | 36 |
| 261.8 | 0.1 | 281000 | 3000 | 1 | 36 |
| 258.4 | 0.1 | 241000 | 3000 | 1.3 | 36 |
| 255.6 | 0.1 | 209000 | 3000 | 1.4 | 36 |
| 252.3 | 0.1 | 177000 | 3000 | 1.7 | 36 |
| 248.4 | 0.1 | 145000 | 3000 | 2.1 | 36 |
| 244.9 | 0.1 | 122000 | 3000 | 2.5 | 36 |
| 272.2 | 0.1 | 462000 | 5000 | 1 | 37 |
| 268.3 | 0.1 | 385000 | 5000 | 1.3 | 37 |
| 265.2 | 0.1 | 336000 | 5000 | 1.5 | 37 |
| 262.5 | 0.1 | 290000 | 5000 | 1.7 | 37 |
| 246.30 | 0.02 | 127973 | 968 | 0.8 | this work |
| 241.25 | 0.02 | 99163 | 965 | 1 | this work |
| 231.16 | 0.02 | 55950 | 187 | 0.3 | this work |
| 221.19 | 0.02 | 30610 | 861 | 2.8 | this work |
| 211.22 | 0.02 | 15038 | 193 | 1.3 | this work |
| 201.14 | 0.02 | 7172 | 144 | 2 | this work |
| 191.12 | 0.02 | 3081 | 59 | 1.9 | this work |
| 181.13 | 0.02 | 1211 | 25 | 2 | this work |
| 171.12 | 0.02 | 422 | 12 | 2.8 | this work |
| 166.13 | 0.02 | 241 | 7.9 | 3.3 | this work |
| 161.08 | 0.02 | 131 | 8.5 | 6.5 | this work |

pressure empirical law expression of Miller (1961)[39] shows a progressive deviation from our relation with a maximum of about 10 % at 151 K.

From the slope of our empirical law, $\Delta H$ is approximately 22.65 kJ·mol$^{-1}$, while the value obtained from the slope of Miller (1961)[39] is 22.3 kJ·mol$^{-1}$. As no calorimetric data are available in the literature, we cannot assess the reliability of our data.

**Comparison with the Empirical Correlation Laws Used in Astrophysical Models.** In this section, we compare the empirical laws used in astrophysical models from (40 to 270) K (temperature range of applications of these laws) to our empirical correlation laws for clathrates of Kr, C$_2$H$_6$, and C$_2$H$_2$. Figure 8 shows the extrapolations of equilibrium pressure empirical laws of single guest clathrates of Kr, C$_2$H$_6$, and C$_2$H$_2$ given in astrophysical papers (lower panel) and presents absolute deviations from our empirical relations (upper panel) as a function of the temperature from (40 to 270) K. For the clathrate of Kr, the expression used in astrophysical models[16] show a deviation from our relation of (4 to 21000) % in this temperature range. For the clathrate of C$_2$H$_2$, the pressure
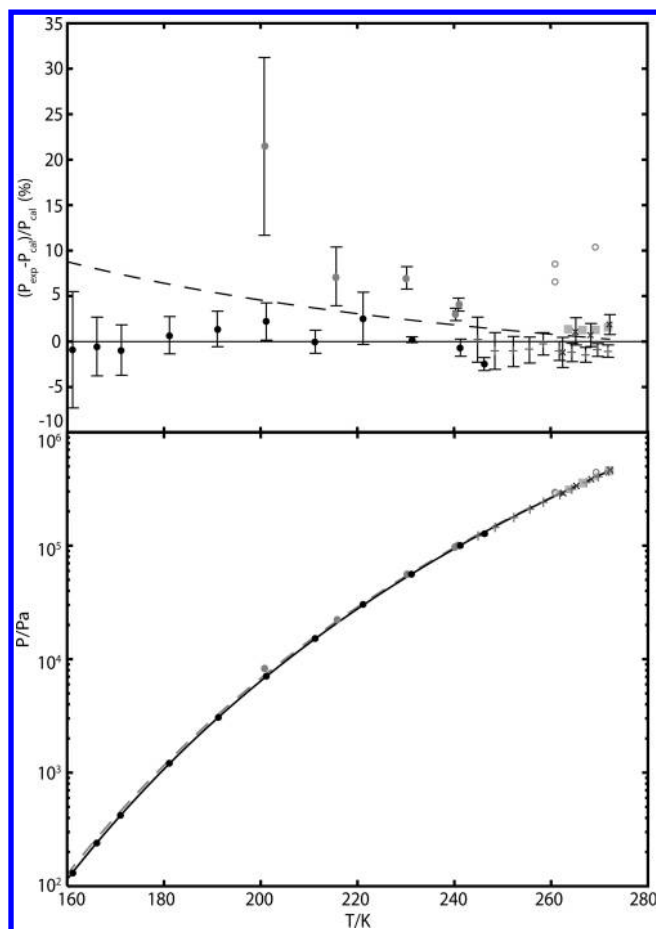
**Figure 5.** Equilibrium pressure of single guest clathrate of $C_2H_6$ (lower panel) and deviations of experimental data from our empirical relation (upper panel) as a function of the temperature: ●, this work; ×, Mohammadi and Richon (2010);[37] +, Yasuda and Ohmura (2008);[36] gray ●, Falabella and Vanpee (1974);[33] gray ■, Deaton and Frost (1946);[35] ○, Roberts et al. (1940);[34] solid black line, our empirical relation; dashed gray line, empirical relation from Miller (1961).[39]
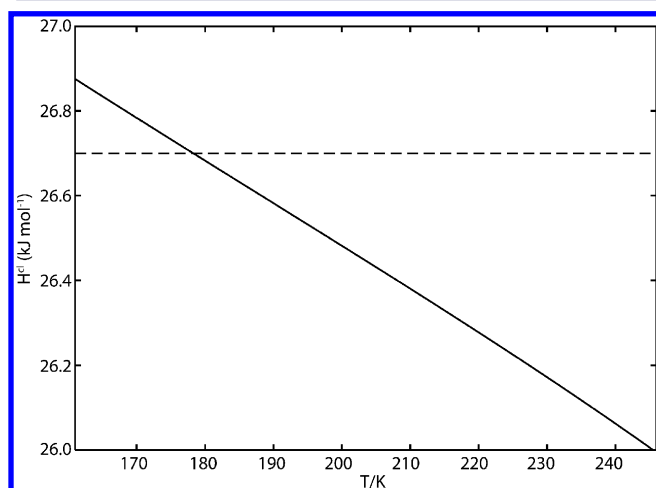


**Figure 6.** Enthalpy of clathrate dissociation of $C_2H_6$ as a function of temperature in the temperature range (151 to 230) K of our data: dashed black line, our value; black line, relation from Handa (1986).[40] Our value is obtained from the $P(T)$ slope of our data and by using eq 3.

**Table 6. Experimental Data for the Equilibrium Pressure of Single Guest Clathrate of $C_2H_2$**

| $T/K$ | $\Delta T/K$ | $P/Pa$ | $\Delta P/Pa$ | $\Delta P/P$ (%) | reference |
|---|---|---|---|---|---|
| 273.15 | unknown | 570000 | unknown | unknown | 38 |
| 257.75 | unknown | 100000 | unknown | unknown | 38 |
| 230.90 | 0.02 | 89845 | 92 | 0.1 | this work |
| 221.09 | 0.02 | 52795 | 213 | 0.4 | this work |
| 211.12 | 0.02 | 29835 | 299 | 1 | this work |
| 201.05 | 0.02 | 15794 | 105 | 0.67 | this work |
| 191.04 | 0.02 | 7683.7 | 64 | 0.84 | this work |
| 181.04 | 0.02 | 3436.4 | 94 | 2.74 | this work |
| 170.97 | 0.02 | 1427.5 | 22 | 1.52 | this work |
| 161.03 | 0.02 | 526.5 | 14 | 2.66 | this work |
| 156.00 | 0.02 | 309.8 | 8 | 2.54 | this work |
| 150.56 | 0.02 | 168.4 | 5 | 2.94 | this work |
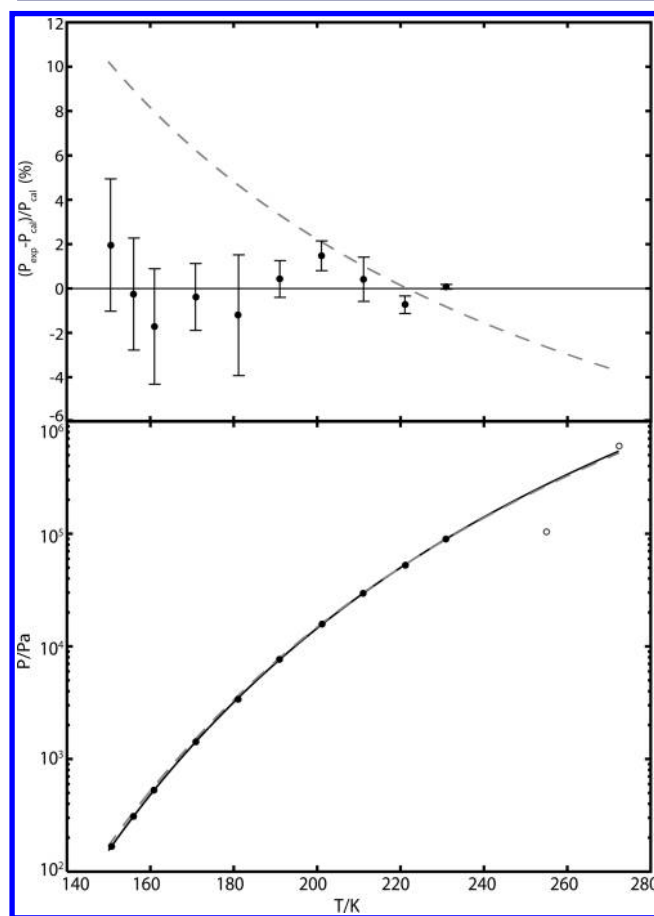


**Figure 7.** Equilibrium pressure of single guest clathrate of $C_2H_2$ (lower panel) and deviations of experimental data from our empirical relation (upper panel) as a function of the temperature: ●, this work; ○, Stackelberg and Müller (1954);[38] solid black line, our empirical relation; dashed gray line, empirical relation from Miller (1961).[39]

empirical law expression of Miller (1961)[39] shows a progressive deviation from our relation of (0 to 150) % in the same range of temperature. For the clathrate of $C_2H_6$, the expression of Miller (1961)[39] and the law used by Mousis and Schmitt (2008)[10] show a deviation from our relation of (0.3 to 100) % and (5 to 320) %, respectively.
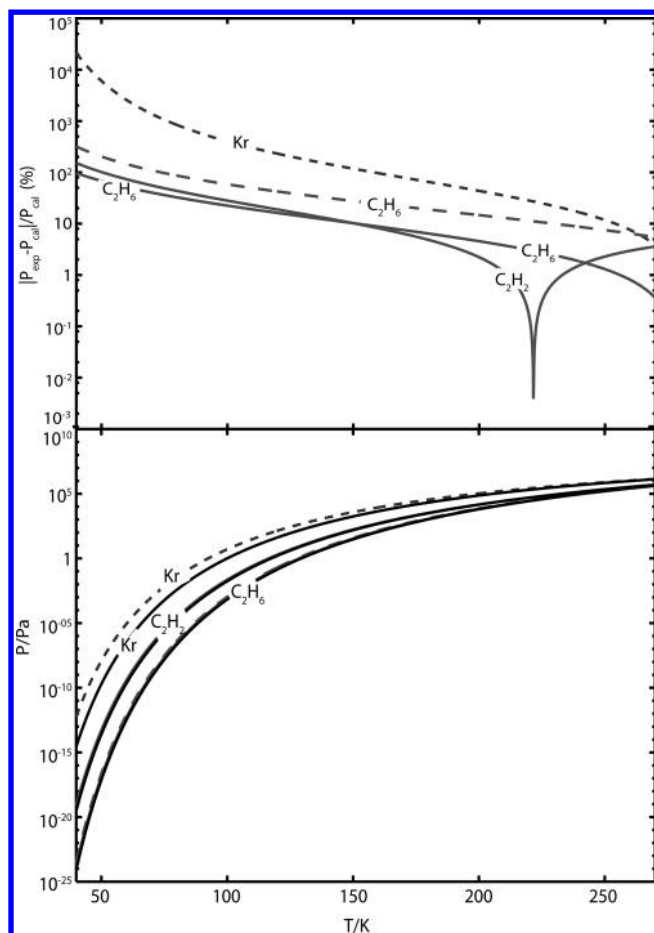
**Figure 8.** Extrapolations of equilibrium pressure empirical laws of single guest clathrate of Kr, $C_2H_6$, and $C_2H_2$ given in astrophysical papers (lower panel) and their deviations from our empirical relation (upper panel) as a function of the temperature from (40 to 270) K. Solid black line, empirical relations determined in this work for Kr, $C_2H_6$, and $C_2H_2$ species; solid gray lines, empirical relation from Miller (1961)[39] for $C_2H_6$ and $C_2H_2$ molecules; dashed black line, empirical relation used by Hersant et al. (2004)[16] for Kr species; dashed gray line, empirical relation used by Mousis and Schmitt (2008)[10] for $C_2H_6$ molecule.

## CONCLUSION

We performed measurements of the equilibrium pressure of single guest clathrates of krypton from (150.97 to 230.45) K, ethane from (161.08 to 246.3) K, and acetylene from (150.56 to 230.90) K. We derived empirical correlation laws allowing to calculate the equilibrium pressure of single guest clathrates of these three species at any temperature below the freezing point of water.

For krypton, our clathrate equilibrium pressures are lower than those published in the literature. We have shown that the data of Barrer and Edge (1967)[30] present a progressive deviation from our measurements and those of Jin et al. (2011).[29] This discrepancy with data of Barrer and Edge (1967)[30] has already been observed with the clathrate of Xe,[22] indicating that their data are not reliable. Moreover, our data and those of Jin et al. (2011)[29] show a systematic deviation so that the three data sets available for the krypton clathrate equilibrium pressure do not converge in a common relationship. Consequently, we have taken into account only our measurements for the determination of the empirical relation

for the equilibrium pressure of this clathrate. For $C_2H_6$, our data set is in good agreement with those of Deaton and Frost (1946),[35] and recent papers of Yasuda and Ohmura (2008),[36] and Mohammadi and Richon (2010),[37] and demonstrates also the reliability of our experimental method. The empirical correlation law of Miller (1961),[39] from unpublished experimental data, shows a progressive deviation from our relation. For $C_2H_2$, the data of Stackelberg and Müller (1954)[38] show a large deviation from our measurements and the equilibrium empirical law given by Miller (1961).[39] We have then taken into account only our measurements for the determination of the equilibrium pressure of this clathrate. The expression of Miller (1961),[39] from unpublished measurements, also shows a low progressive deviation from our data.

For the three species, we calculated the enthalpy of clathrate dissociation $\Delta H$ using the Clausius–Clapeyron equation. Our results agree well with the $\Delta H$ values obtained from calorimetric measurements of ethane[40] and krypton,[31] but there are no published data for acetylene. These new empirical laws could affect theoretical studies on the clathrate formation/dissociation in extraterrestrial environments (e.g., comets and icy moons of the solar system) since the laws currently used in astrophysical models show significant deviations from our results.

## ■ AUTHOR INFORMATION

**Corresponding Author**
*E-mail: marboeuf@ujf-grenoble.fr.

**Notes**
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

## ■ REFERENCES

(1) Delsemme, A. H.; Swings, P. Hydrates de gaz dans les noyaux cométaires et les grains interstellaires. *Ann. Astrophys.* 1952, *15*, 1−6.
(2) Klinger, J.; Ocampo, J.; Schmitt, B. On clathrate hydrates in comets. *Asteroids, Comets, Meteors II* 1986, 241−243.
(3) Schmitt, B.; Klinger, J. Different trapping mechanisms of gases by water ice and their relevance for comet nuclei. in Diversity and Similarity of Comets. *ESA Spec. Publ.* 1987, *278*, 613−619.
(4) Smoluchowski, R. Clathrate hydrates in cometary nuclei and porosity. *Month, Not. Roy. Astrom. Soc.* 1988, *235*, 343−348.
(5) Mousis, O.; Gautier, D.; Bockelée-Morvan, D.; Robert, F.; Dubrulle, B.; Drouart, A. Constraints on the Formation of Comets from D/H Ratios Measured in $H_2O$ and HCN. *Icarus* 2000, *148*, 513−525.
(6) Prialnik, D.; Benkhoff, J.; Podolak, M. Modeling the structure and activity of comet nuclei. *Comets II* 2004, 359−387.
(7) Huebner, W. F. Origins of Cometary Materials. *Space Sci. Rev.* 2008, *138*, 5−25.
(8) Marboeuf, U.; Mousis, O.; Petit, J.-M.; Schmitt, B. Clathrate Hydrates Formation in Short-Period Comets. *Astrophys. J.* 2010, *708*, 812−816.

(9) Marboeuf, U.; Mousis, O.; Petit, J.-M.; Schmitt, B.; Cochran, A. L.; Weaver, H. A. On the stability of clathrate hydrates in comets 67P/Churyumov-Gerasimenko and 46P/Wirtanen. *Astronomy Astrophys.* **2011**, *525*, A144.

(10) Mousis, O.; Schmitt, B. Sequestration of Ethane in the Cryovolcanic Subsurface of Titan. *Astrophys. J.* **2008**, *677*, L67−L70.

(11) Lewis, J. S. Low Temperature Condensation from the Solar Nebula. *Icarus* **1972**, *16*, 241−252.

(12) Gautier, D.; Hersant, F.; Mousis, O.; Lunine, J. I. Enrichments in Volatiles in Jupiter: A New Interpretation of the Galileo Measurements. *Astrophys. J.* **2001**, *550*, L227−L230.

(13) Gautier, D.; Hersant, F.; Mousis, O.; Lunine, J. I. Erratum: Enrichments in Volatiles in Jupiter: A New Interpretation of the Galileo Measurements. *Astrophys. J.* **2001**, *559*, L183−L183.

(14) Iro, N.; Gautier, D.; Hersant, F.; Bockelée-Morvan, D.; Lunine, J. I. An interpretation of the nitrogen deficiency in comets. *Icarus* **2003**, *161*, 511−532.

(15) Loveday, J. S.; Nelmes, R. J.; Guthrie, M.; Belmonte, S. A.; Allan, D. R.; Klug, D. D.; Tse, J. S.; Handa, Y. P. Stable methane hydrate above 2 GPa and the source of Titan's atmospheric methane. *Nature* **2001**, *410*, 661−663.

(16) Hersant, F.; Gautier, D.; Lunine, J. I. Enrichment in volatiles in the giant planets of the Solar System. *Planet. Space Sci.* **2004**, *52*, 623−641.

(17) Mousis, O.; Lunine, J. I.; Picaud, S.; Cordier, D. Volatile inventories in clathrate hydrates formed in the primordial nebula. *Faraday Discuss.* **2010**, *147*, 509−525.

(18) Mousis, O.; Marboeuf, U.; Lunine, J. I.; Alibert, Y.; Fletcher, L. N.; Orton, G. S.; Pauzat, F.; Ellinger, Y. Determination of the Minimum Masses of Heavy Elements in the Envelopes of Jupiter and Saturn. *Astrophys. J.* **2009**, *696*, 1348−1354.

(19) Blake, D.; Allamandola, L.; Sandford, S.; Hudgins, D.; Freund, F. Clathrate Hydrate Formation in Amorphous Cometary Ice Analogs in Vacuo. *Science* **1991**, *254*, 548−551.

(20) Bockelée-Morvan, D.; Crovisier, J.; Mumma, M. J.; Weaver, H. A. The Composition of Cometary Volatiles. *Comets II* **2004**, 391.

(21) Dauphas, N. The dual origin of the terrestrial atmosphere. *Icarus* **2003**, *165*, 326−339.

(22) Fray, N.; Marboeuf, U.; Brissaud, O.; Schmitt, B. Equilibrium Data of Methane, Carbon Dioxide, and Xenon Clathrate Hydrates below the Freezing Point of Water. Applications to Astrophysical Environments. *J. Chem. Eng. Data* **2010**, *55*, 5101−5108.

(23) Barrer, R. M.; Ruzicka, D. J. Non-stoichiometric clathrate compounds of water. Part 4.-Kinetics of formation of clathrate phases. *Trans. Faraday Soc.* **1962**, *58*, 2262−2271.

(24) Bar-Nun, A.; Dror, J.; Kochavi, E.; Laufer, D. Amorphous water ice and its ability to trap gases. *Phys. Rev. B* **1987**, *35*, 2427−2435.

(25) Kim, H. C.; Bishnoi, P. R.; Heidemann, R. A.; Rizvi, S. S. H. Kinetics of methane hydrate decomposition. *Chem. Eng. Sci.* **1987**, *42*, 1645−1653.

(26) Englezos, P.; Kalogerakis, N.; Dholabhai, P. D.; Bishnoi, P. R. Kinetics of formation of methane and ethane gas hydrates. *Chem. Eng. Sci.* **1987**, *42*, 2647−2658.

(27) Clarke, M. A.; Bishnoi, P. R. Determination of the intrinsic rate constant and activation energy of $CO_2$ gas hydrate decomposition using in-situ particle size analysis. *Chem. Eng. Sci.* **2004**, *59*, 2983−2993.

(28) Sun, X.; Mohanty, K. K. Kinetic simulation of methane hydrate formation and dissociation in porous media. *Chem. Eng. Sci.* **2006**, *61*, 3476−3495.

(29) Jin, Y.; Matsumoto, K.; Nagao, J.; Shimada, W. Phase Equilibrium Conditions for Krypton Clathrate Hydrate below the Freezing. *J. Chem. Eng. Data* **2011**, *56*, 58−61.

(30) Barrer, R. M.; Edge, A. V. J. Gas hydrates containing argon, krypon and xenon: kinetics and energetics of formation and equilibria. *Proc. R. Soc. London A* **1967**, *300*, 1−24.

(31) Handa, Y. P. Calorimetric determinations of the compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of xenon and krypton. *J. Chem. Thermodyn.* **1986**, *18*, 891−902.

(32) Makogon, T. Y.; Sloan, E. D. Phase Equilibrium for Methane Hydrate from 190 to 262 K. *J. Chem. Eng. Data* **1994**, *39*, 351−353.

(33) Falabella, B. J.; Vanpee, M. Experimental Determination of Gas Hydrate Equilibrium below the Ice Point. *Ind. Eng. Chem. Fundam.* **1974**, *13*, 228−231.

(34) Roberts, O. L.; Brownscombe, E. R.; Howe, L. S.; Ramser, H. Constitution Diagrams and Composition of Methane and Ethane Hydrates. *Oil Gas J.* **1940**, *39*, 37−41.

(35) Deaton, W. M.; Frost, E. M. Gas Hydrates and Their relation to Operation of Natural-Gas Pipelines. *U. S. Bur. Mines, Monogr.* **1946**, *8*, 1−101.

(36) Yasuda, K.; Ohmura, R. Phase Equilibrium for Clathrate Hydrates Formed with Methane, Ethane, Propane, or Carbon Dioxide at Temperatures below the Freezing Point of Water. *J. Chem. Eng. Data* **2008**, *53*, 2182−2188.

(37) Mohammadi, A. H.; Richon, D. Ice-Clathrate Hydrate-Gas Phase Equilibria for Air, Oxygen, Nitrogen, Carbon Monoxide, Methane, or Ethane plus Water System. *Ind. Eng. Chem. Res.* **2010**, *48*, 3976−3979.

(38) Stackelberg, M. v.; Müller, H. R. Feste Gashydrate II struktur und Raumchemie. *Z. Elektrochem.* **1954**, *58*, 25−39.

(39) Miller, S. L. The occurrence of gas hydrates in the solar system. *Proc. Natl. Acad. Sci. U.S.A.* **1961**, *47*, 1798−1808.

(40) Handa, Y. P. Compositions, enthalpies of dissociation, and heat capacities in the range 85 to 270 K for clathrate hydrates of methane, ethane, and propane, and enthalpy of dissociation of isobutane hydrate, as determined by a heat-flow calorimeter. *J. Chem. Thermodyn.* **1986**, *18*, 915−921.

(41) Marboeuf, U.; Schmitt, B.; Petit, J.-M.; Mousis, O.; Fray, N. A cometary nucleus model taking into account all phase changes of water ice: amorphous, crystalline, and clathrate. *Astonomy Astrophys.* **2012**, *542*, A82.

(42) Chao, J.; Wilhoit, R. C.; Zwolinski, B. J. Ideal gas thermodynamic properties of Ethane and Propane. *J. Phys. Chem. Ref. Data* **1973**, *2*, 427−437.