J. Chem. Eng. Data **2010,** *55,* 5101–5108 **5101**

Equilibrium Data of Methane, Carbon Dioxide, and Xenon Clathrate Hydrates below the Freezing Point of Water. Applications to Astrophysical Environments

Nicolas Fray,*[†,‡] Ulysse Marboeuf,[†] Olivier Brissaud,[†] and Bernard Schmitt[†]

Laboratoire de Planétologie de Grenoble, Université Joseph Fourier, CNRS/INSU, Bâtiment D de Physique,
BP 53, 38041 Grenoble Cedex 9, France, and LISA, Laboratoire Interuniversitaire des Systèmes Atmosphériques,
UMR 7583 du CNRS, Universités Paris 7 et 12, 61 Avenue du Général de Gaulle, 94010 Créteil Cedex, France

This work reports new measurements of the three-phase (ice + clathrate hydrate + vapor) equilibrium in the systems of water and each of the following guest species: xenon from (167.20 to 246.16) K, carbon dioxide from (172.28 to 182.15) K, and methane from (145.75 to 195.74) K. The results are compared with the corresponding data reported in the literature and are used to determine empirical laws allowing the equilibrium pressure of these pure clathrates to be calculated at any temperature relevant to the astrophysical environments below the freezing point of water. These relations can be used in astrophysical models such as those devoted to the studies of the cooling and condensation of the solar nebula or to the ones of the physical evolution and gas production from cometary nuclei.

Introduction

Clathrate hydrates are water-based solid crystalline compounds stabilized by the inclusion of guest molecules inside cavities formed by the hydrogen-bonded network of water molecules.[1] They resemble ice in appearance, but they may form at temperatures higher than the freezing temperature of water. They are of great interest in the natural gas industry, as they can plug pipelines and flow channels. Some natural clathrate hydrates have also been discovered on Earth: in the seafloor, in permafrost, as well as in polar caps.[1,2] The amount of methane potentially trapped in natural methane clathrate hydrate deposits, mostly in seafloor sediments, may be very significant (from 1 to $5 \cdot 10^{15}$ m^3), which makes them of major interest as a potential energy resource. Although no clathrate hydrate has been detected so far in astrophysical environments, it has been proposed for a long time that clathrate hydrates could play a significant role in the chemistry of the solar nebula and in the physical evolution of numerous astrophysical objects.[3−7]

As it is of interest for the natural gas industry and for the studies of clathrate hydrates present in the seafloor, the L_W-H-V three-phase equilibrium (liquid water (L_W) + clathrate hydrate (H) + guest vapor (V)) of simple or mixed clathrate hydrates at temperatures higher than the freezing temperature of water has been extensively studied. Nevertheless, in the astrophysical environments, the temperature is very low compared to the freezing temperature of water. Thus, L_W-H-V equilibrium data are not relevant for most astrophysical applications. The $I-H-V$ three-phase equilibrium (water ice (I) + clathrate hydrates (H) + guest vapor (V)) for clathrate hydrates at temperatures below the freezing temperature of water is important for most astrophysical studies such those of the cooling and condensation of the solar nebula, cometary nuclei, Titan hydrocarbon reservoirs, or Mars polar caps. Despite the importance of the phase equilibrium data at temperatures below the freezing temperature of water, there is a paucity of data in contrast to the ones at temperatures above the freezing temperature of water.

Delsemme and Swings[6] were the first to consider the presence of clathrate hydrates in the outer solar system and in cometary nuclei. Then, Miller[7] argued that clathrate hydrates could be present on most of the objects of the outer solar system as they incorporate molecular species at vapor pressures lower than those of the pure ices of those species. Lewis[8] and Sill and Wilkening[9] seem to be the first to investigate the possible formation of clathrate hydrates during the cooling of the solar nebula. Indeed when the temperature of the solar nebula decreases, water vapor condenses at about 150 K and forms microscopic icy particles. During the subsequent cooling, clathrate hydrates of H_2S, CH_4, Xe, CO, N_2, Kr, and Ar should form before these gaseous compounds could condense as pure ices.[10,11] Models of the cooling of the solar nebula taking into account the formation of clathrate hydrates succeed to reproduce the elemental enrichments observed in the four giant planets[10,12] as well as the nitrogen deficiency in comets.[11] So, if formed during the cooling of the solar nebula, clathrate hydrates could be indeed present in most objects of the outer solar system. Moreover, some clathrate hydrates could have been formed during the evolution of these objects; it could be the case of methane, ethane, and xenon clathrate hydrates at the surface of Titan,[13,14] carbon dioxide clathrate hydrates in polar caps of Mars,[15] and carbon monoxide clathrate hydrates in cometary nuclei.[16] We have to keep in mind that no clathrate hydrate has been detected so far in astrophysical environments and that all of the predictions concerning the possible presence of clathrates in astrophysical objects are based on extrapolations at very low temperatures of the few $I-H-V$ equilibrium data.

In this paper, we report measurements of the $I-H-V$ equilibrium pressure at low temperatures for single guest molecular (hereafter single) clathrate hydrates of xenon, carbon dioxide, and methane. We also determine empirical relations allowing

---

* Corresponding author. E-mail: nicolas.fray@lisa.u-pec.fr. Tel.: 00 33 (0)1 45 17 15 56. Fax: 00 33 (0)1 45 17 15 64.

[†] Laboratoire de Planétologie de Grenoble. E-mail: marboeuf@ujf-grenoble.fr, olivier.brissaud@obs.ujf-grenoble.fr, bernard.schmitt@obs.ujf-grenoble.fr.

[‡] LISA.

10.1021/je1006604

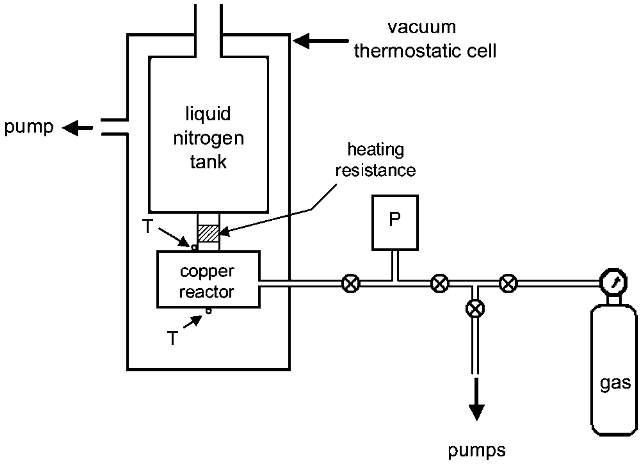

Figure 1. Schematic diagram of the apparatus used to measure the equilibrium pressure of xenon, carbon dioxide, and methane clathrate hydrates.

us to calculate the equilibrium pressure of clathrate hydrates at any temperatures relevant to the different astrophysical environments.

Experimental Section

Apparatus. A schematic diagram of our apparatus is shown in Figure 1. A cylindrical copper reactor of 26 mm internal diameter and of about 13 cm^3 inner volume is used to measure the equilibrium pressure of clathrate hydrates. It is composed of two 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 thanks to 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 this copper finger, and two silicon diodes, allowing us to measure the temperature from (70 to 300) K with an uncertainty of about 0.01 K, are glued on the lower and upper parts of the reactor. The heating resistance and both silicon diodes are connected to a temperature controller (model 331 of Lakeshore), which ensures a temperature stability of about ± 0.03 K.

The reactor is evacuated thanks to 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 an absolute metal membrane pressure sensor (Baratron 690-A13T-RB, MKS) allowing us to measure the pressure between 1 Pa and 133.3 kPa with a resolution of 0.1 Pa and a relative uncertainty of 0.08 % of the reading value over most of the range over 100 Pa. Temperature and pressure are recorded as a function of time with a resolution of a few seconds thanks to a laboratory-made software.

Note that our reactor includes neither a stirrer nor a shaker contrary to most experimental setups devoted to the measurement of the I−H−V equilibrium.[17−20] Normally, these devices are used to crush the sample of ice and clathrate hydrates and to activate the kinetics of clathrate hydrate formation.[17]

Materials. The water used in the experiments was laboratory deionized and distilled and has a resistivity of 18.2 $M\Omega \cdot cm$. All of the gases have been purchased from Air Liquide; xenon, carbon dioxide, and methane have certified volume fraction purities of 99.998 %, 99.998 %, and 99.95 %, respectively.

Procedure. We have tried to reproduce in the laboratory the astrophysical process of clathrate hydrates formation, that is, we have tried to form clathrate hydrates directly from crystalline ice submitted to an overpressure of gas (but < 100 kPa). Nevertheless, as our reactor is neither equipped with a stirrer nor a shaker, our attempts of forming clathrate hydrates from crystalline ice have failed. We attribute this failure to a very long nucleation stage as already observed by Schmitt[21] and Moudrakovski et al.[22]

Thus, we choose to form clathrate hydrates in a second reactor in which we introduce about 5 cm^3 of liquid water and about 200 kPa of Xenon. This reactor is then immersed in a bath at 1 °C within a few minutes, and we obtain about 1 g of xenon clathrate hydrate which sinks in liquid water. These xenon clathrate hydrates are then transferred in the copper reactor, and the apparatus is reassembled. This transfer is performed under ambient atmosphere and in a cold room at −20 °C to slow down the decomposition of the Xe clathrate hydrate.

The study of the carbon dioxide or methane clathrate hydrates involves the conversion of our initial sample of xenon clathrate hydrate to carbon dioxide or methane clathrate hydrate. Such a transformation of one clathrate hydrate to another guest clathrate hydrate has already been performed and studied by Yoon et al.[23] In such a case, the copper reactor is thermostatted at the temperature corresponding to an equilibrium pressure of the desired clathrate hydrate of about 90 kPa. First, the gaseous xenon is evacuated, and we pump during about 1 min on the solid sample of clathrate hydrate. Second, we inject an overpressure of carbon dioxide or methane in the reactor. A rapid pressure decrease, due to the formation of clathrate hydrate of the guess molecule, is observed, and we wait for pressure stabilization. In this case, the nucleation stage is practically absent, and the clathrate hydrate growth begins very rapidly. This behavior was observed by Schmitt[21] and Moudrakovski et al.[22] and was interpreted as a preorganization of the ice surface. Indeed, after the evacuation of xenon, some cages should remain empty, and the overpressure of gas was injected before the transformation of the empty cages into crystalline water ice. This operation is repeated at least 10 times to ensure the removal of almost all of the initial xenon. If some xenon atoms remain after this, it should be only located deep inside the grains without contact with the gas phase and thus without influence on the equilibrium pressure of the newly formed clathrate nor contribution to the gas pressure.

When a sample of pure clathrate hydrate of the desired species (xenon, carbon dioxide, or methane) is obtained, the temperature of the copper cell is maintained constant, and an overpressure of gas is injected in the reactor. A pressure decrease is observed, as shown in Figure 2, due to the formation of clathrate hydrates and encapsulation of the gas molecules. The pressure should converge toward the equilibrium pressure; nevertheless, an apparent stabilization at higher pressures could be observed. This stabilization could be due either to the inclusion of all available water molecules into the clathrate hydrate structure and thus deviation of our measurements from the I−H−V equilibrium (no more ice) or to the formation of a thick impermeable layer of clathrate hydrate on the ice grains[21] also removing water ice from the I−H−V equilibrium. In such cases it is necessary to partially decompose the clathrate hydrates to form enough ice to go back to the I−H−V phase equilibrium. After obtaining the true clathrate equilibrium from a higher pressure, we reduce the pressure below the equilibrium pressure. A pressure increase is rapidly observed due to the decomposition of clathrate hydrates and the release of gas molecules. This procedure is repeated several times. A similar procedure has been used by different authors[24,25] at higher temperatures.

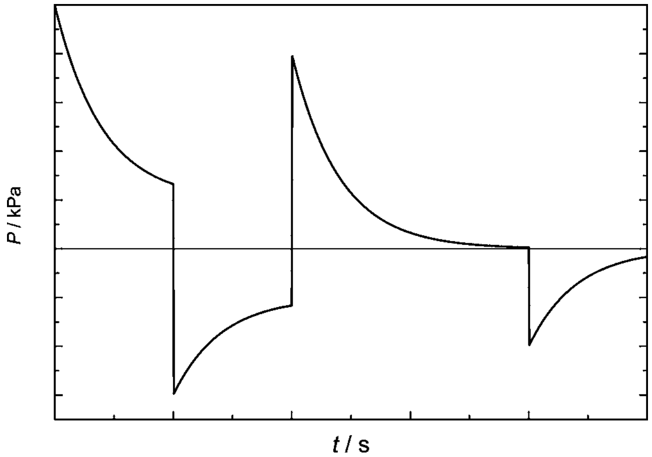

Figure 2. Schematic diagram of the experimental procedure at constant temperature.

At low temperatures such the ones that we have explored, the kinetic of clathrate hydrate formation or decomposition is extremely slow, and therefore it is very difficult to reach the equilibrium as schematized in Figure 2. Nevertheless, it has already been shown[21] that when the pressure comes close to its equilibrium value, it follows the following equation:

$$\frac{dP}{dt} = k(P - P_{\mathrm{eq}}) \tag{1}$$

where k is the kinetic constant in s^{-1} and P_{eq} the equilibrium pressure. For the whole measured pressure evolution, we have determined the time range on which the slope (dP/dt) varies linearly against the pressure. Then, for this time range, the pressure evolution has been adjusted and extrapolated using the following equation:

$$P(t) = P_{\mathrm{eq}} + \Delta P \cdot e^{-k(t-t_o)} \tag{2}$$

It allows us to determine the value to which the pressure tends. The equilibrium pressure is supposed to be the arithmetic average of the two closest values of decomposition and formation pressures, while the uncertainty is supposed to be the difference between these two values. An example of this procedure is given in Figure 3.

In most cases, the formation and the decomposition curves are observed for the same sample of clathrate hydrate. In these cases, the uncertainty on the temperature is about ± 0.03 K. In a few cases, the formation and decomposition curves were observed for different samples of clathrate hydrate with slightly different temperatures ($\Delta T < 0.5$ K). In such a case, the formation (or decomposition) equilibrium pressure has been corrected to the measurement temperature of the other using the slope dP/dT of the whole equilibrium curve, before averaging both values.

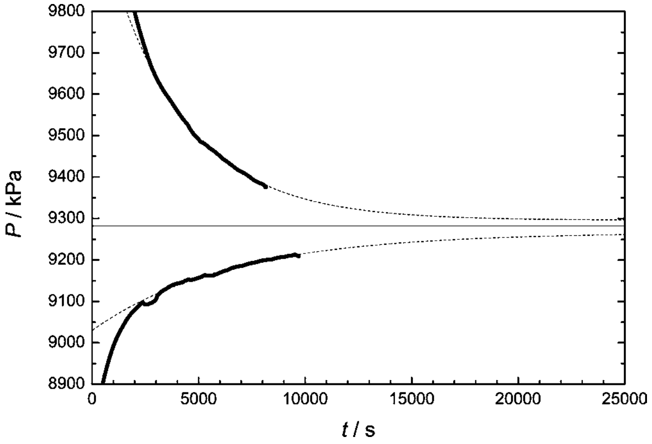

Figure 3. Temporal evolution of the pressure for a sample of xenon clathrate hydrates at $T = (219.53 \pm 0.03)$ K: solid lines, experimental measurements; dotted lines, adjustment and extrapolations of the experimental measurements; gray horizontal line, determined equilibrium pressure.

Table 1. Experimental Data for the HIV Equilibrium of Xenon Clathrate Hydrate

T/K	ΔT/K	P/kPa	ΔP/kPa	100 $\Delta P/P$	ref
268.2	0.1	121.3	0.7	0.6	18
253.3	0.1	64.8	0.7	1.1	18
238.2	0.1	30.8	0.7	2.3	18
229.4	0.1	19.4	0.7	3.6	18
223.0	0.1	13.5	0.7	5.2	18
211.2	0.1	6.5	0.7	10.8	18
273.15	0.2	155.1	7.0	4.5	25
228.15	0.3	16.2	7.0	43.2	25
246.16	0.03	43.67	$5 \cdot 10^{-2}$	0.1	this work
241.33	0.02	33.89	$3 \cdot 10^{-2}$	0.1	this work
228.17	0.02	16.21	$2 \cdot 10^{-2}$	0.1	this work
219.53	0.03	9.28	$1 \cdot 10^{-2}$	0.1	this work
216.60	0.04	7.50	$3 \cdot 10^{-2}$	0.4	this work
212.44	0.08	5.59	$8 \cdot 10^{-2}$	1.4	this work
207.17	0.05	3.85	$9 \cdot 10^{-2}$	2.3	this work
201.18	0.02	2.60	$2 \cdot 10^{-2}$	0.8	this work
191.17	0.02	1.11	$3 \cdot 10^{-3}$	0.5	this work
182.12	0.01	0.48	$3 \cdot 10^{-2}$	6.2	this work
175.84	0.01	0.264	$1.5 \cdot 10^{-3}$	0.6	this work
170.78	0.01	0.157	$1.5 \cdot 10^{-3}$	1.0	this work
167.47	0.03	0.099	$1 \cdot 10^{-3}$	1.0	this work

Results and Discussion

All experimental equilibrium data measured in this work, as well as all the I−H−V experimental data already published in the literature for simple xenon, carbon dioxide, and methane clathrate hydrates are reported in Tables 1, 2, and 3 and are plotted in Figures 4, 5, and 6, respectively. Our measurements are also compared with the empirical laws used in astrophysical models and the pressure predicted by the CSMGem code developed by Sloan and Koh[1] to compute the equilibrium conditions of clathrate hydrates.

All of the experimental measurements are used to determine empirical relations allowing us to calculate the equilibrium pressure of clathrate hydrates at any temperatures below the freezing temperature of water. To fit the experimental measurements, we use the following relation:

$$\ln P = A + B/T \tag{3}$$

in which P and T are the pressure (in kPa) and the absolute temperature. The parameters A and B are given in Table 4. This semiempirical formula can be derived from the Clausius−Clapeyron equation assuming that (i) the molar volume of the condensed phase is negligible against that of the gas, (ii) the gas is perfect, and (iii) the enthalpy of the phase change is independent of the temperature.

Clathrate Hydrate of Xenon. Concerning the xenon clathrate hydrate, we have performed 13 measurements ranging from 167.47 K (0.1 kPa) to 246.16 K (43.7 kPa) given in Table 1 and Figure 4. These data enlarge the temperature range on which the I−H−V equilibrium of xenon clathrate hydrate has been studied, since no data for T lower than 210 K has been reported

Table 2. Experimental Data for the HIV Equilibrium of Carbon Dioxide Clathrate Hydrate

T/K	ΔT/K	P/kPa	ΔP/kPa	100 $\Delta P/P$	ref
271.8	unknown	1048	unknown	unknown	27
271.7	unknown	1041	unknown	unknown	27
271.4	unknown	1027	unknown	unknown	27
270.7	unknown	1000	unknown	unknown	27
270	unknown	972	unknown	unknown	27
268.9	unknown	924	unknown	unknown	27
267.4	unknown	869	unknown	unknown	27
264	unknown	752	unknown	unknown	27
256.8	unknown	545	unknown	unknown	27
192.54	unknown	21.88	unknown	unknown	15
186.75	unknown	14.49	unknown	unknown	15
182.15	unknown	10.27	unknown	unknown	15
176.86	unknown	6.77	unknown	unknown	15
171.54	unknown	4.20	unknown	unknown	15
167.07	unknown	2.808	unknown	unknown	15
162.37	unknown	1.765	unknown	unknown	15
151.52	unknown	0.535	unknown	unknown	15
200.96	unknown	36.3	unknown	unknown	54
200.58	unknown	37.8	unknown	unknown	54
198.99	unknown	33.4	unknown	unknown	54
196.78	unknown	29.3	unknown	unknown	54
218.2	unknown	104.3	unknown	unknown	58
217.8	unknown	101.3	unknown	unknown	58
213.8	unknown	81.6	unknown	unknown	58
203.2	unknown	43.3	unknown	unknown	58
194.5	unknown	24.8	unknown	unknown	58
213.6	0.1	80.4	0.4	0.50	21
208.1	0.1	59.0	0.3	0.50	21
203.1	0.1	43.7	0.2	0.46	21
198.6	0.1	33.8	0.2	0.59	21
195.2	0.1	26.0	0.1	0.38	21
195	0.1	25.7	0.1	0.39	21
271.14	0.1	102.6	5	4.9	33
269.4	0.1	963	11	1.1	19
266.4	0.1	864	11	1.3	19
263.9	0.1	790	11	1.4	19
262.7	0.1	755	11	1.5	19
258.8	0.1	652	11	1.7	19
256.4	0.1	593	11	1.9	19
253	0.1	516	11	2.1	19
249.8	0.1	454	11	2.4	19
247.1	0.1	406	11	2.7	19
244.5	0.1	364	11	3.0	19
271	0.1	1050	5	0.48	20
268.9	0.1	960	5	0.52	20
266.7	0.1	870	5	0.57	20
264.5	0.1	780	5	0.64	20
182.36	0.02	9.9	0.08	*0.8*	this work
176.91	0.02	6.46	0.13	*2.0*	this work
172.28	0.1	4.47	0.40	*8.9*	this work

Table 3. Experimental Data for the HIV Equilibrium of Methane Clathrate Hydrate

T/K	ΔT/K	P/kPa	ΔP/kPa	100 $\Delta P/P$	ref
259.04	unknown	1647.7	unknown	unknown	55
270.9	0.03	2390	15	0.6	17
268.6	0.03	2220	15	0.7	17
266.5	0.03	2080	15	0.7	17
264.2	0.03	1900	15	0.8	17
262.4	0.03	1790	15	0.8	17
111	unknown	$1.87 \cdot 10^{-2}$	$5.3 \cdot 10^{-3}$	28	35
106	unknown	$8.67 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	23	35
100	unknown	$2.13 \cdot 10^{-3}$	unknown	unknown	35
97	unknown	$1.23 \cdot 10^{-3}$	unknown	unknown	35
94	unknown	$6.27 \cdot 10^{-4}$	unknown	unknown	35
91	unknown	$2.67 \cdot 10^{-4}$	unknown	unknown	35
88	unknown	$1.40 \cdot 10^{-4}$	unknown	unknown	35
85	unknown	$7.33 \cdot 10^{-5}$	unknown	unknown	35
82	unknown	$2.13 \cdot 10^{-5}$	unknown	unknown	35
193.2	0.05	101.3	0.67	0.7	34
191.3	0.05	90.1	0.67	0.7	34
178.2	0.05	42	0.67	1.6	34
168.8	0.05	21.1	0.67	3.2	34
159.9	0.05	12.1	0.67	5.5	34
148.8	0.05	5.3	0.67	12.6	34
190.15	0.1	84.71	1.7	2.0	56
198.15	0.1	134.9	2.7	2.0	56
208.15	0.1	227.8	4.6	2.0	56
218.15	0.1	366.6	7.3	2.0	56
243.15	0.1	980.5	20	2.0	56
262.4	0.1	1847	37	2.0	56
272.2	0.1	2471	11	0.5	19
269.1	0.1	2236	11	0.5	19
265.5	0.1	2008	11	0.5	19
262.6	0.1	1829	11	0.6	19
259.1	0.1	1634	11	0.7	19
257.1	0.1	1518	11	0.7	19
256.3	0.1	1485	11	0.7	19
252.9	0.1	1324	11	0.8	19
248.8	0.1	1155	11	1.0	19
245.9	0.1	1041	3	0.3	19
244.2	0.1	971	3	0.3	19
272.6	0.1	2521	5	0.2	57
269.4	0.1	2269	5	0.2	57
265.2	0.1	1985	5	0.3	57
263.2	0.1	1842	5	0.3	57
195.74	0.02	103.2	1.2	1.1	this work
190.83	0.02	78.6	0.7	0.9	this work
180.82	0.02	41.7	0.8	1.9	this work
170.82	0.01	20.5	0.8	3.9	this work
160.87	0.05	8.8	0.2	2.3	this work
145.75	0.01	2.4	0.2	8.3	this work

before. Our measurements fit smoothly with the previous results of Makogon et al.,[25] but we observe a progressive deviation from the ones of Barrer and Edge[18] at lower temperature. No particular reason has been found to explain this deviation, except possibly a constant positive bias of about 1.5 kPa in their data (about two times their stated uncertainty). Whereas the data of Barrer and Edge[18] are not necessarily erroneous, we have rejected them, and we take into account only our measurements and the ones of Makogon et al.[25] for the determination of our empirical relation. It reproduces our experimental measurements and the two ones of Makogon et al.[25] with a relative deviation better than ± 6 %. The empirical relations previously used in astrophysical models[12,26] were based on the measurements of Barrer and Edge;[18] thus, they present the same erroneous deviation. At about 140 K, the predicted pressure is already twice than the one predicted using our empirical relation. The CSMGem code converges only for temperatures higher than 240 K. In the (240 to 273) K temperature range, the equilibrium pressures computed with this code display a slight relative deviation of ± 3 %, and the slope of this $P(T)$ curve seems to be too weak.

Because of the paucity of data about the L_W−H−V equilibrium for xenon clathrate hydrates, no determination of the Q1 quadruple point has been performed.

Clathrate Hydrate of Carbon Dioxide. Concerning carbon dioxide clathrate hydrates, we have performed three measurements ranging from 172.28 K (4.5 kPa) to 182.36 K (9.9 kPa) and shown in Figure 5 and Table 2. Our measurements fit smoothly with all of the previous results and particularly with the ones of Miller and Smythe[15] which have been performed in the same temperature range. This agreement shows that our experimental procedure is correct and that, if any xenon clathrate hydrate is remaining, it has no influence on the carbon dioxide clathrate hydrate equilibrium. To compute the empirical relation, we take into account all data reported in the literature. This relation reproduces all of the experimental measurements with a relative deviation better than ± 10 % and most of them within ± 4 %. It can be noted that the data set of Larson[27] and the one of Mohammadi and Richon[20] present a slope which seems to be much too large. We have checked that these data have not

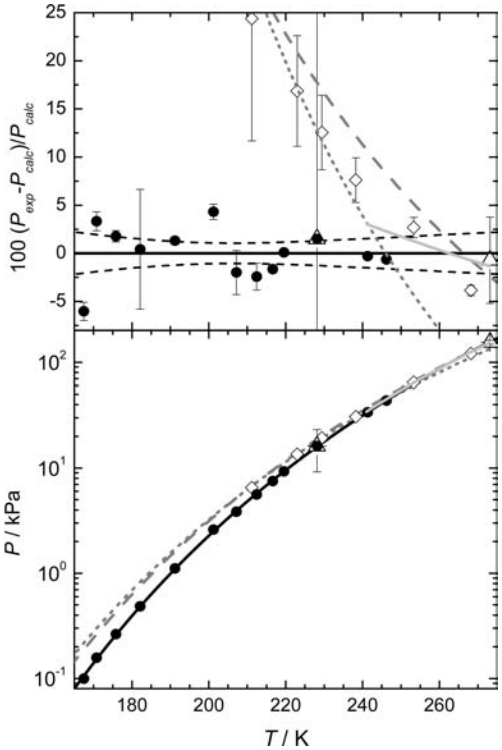

Figure 4. Equilibrium pressure of xenon clathrate hydrates as a function of the temperature for the HIV three-phase equilibrium (lower panel) and deviations of the experimental equilibrium pressures from those calculated by the empirical relation (upper panel): ●, this work; ◇, Barrer and Edge;[18] △, Makogon et al.;[25] solid black line, empirical relation determined in this work; dotted black line, confidence band at 95 % of our empirical relation; solid gray line, CSMGem prediction;[1] dashed gray line, empirical relation used by Hersant et al.;[12] dotted gray line, empirical relation used by Thomas et al.[26]

been acquired with liquid water in surfusion and correspond really to the I−H−V equilibrium. But our data are very consistent with those of Yasuda and Ohmura.[19] The empirical relations previously used in astrophysical models are the ones of Miller[7] and Miller and Smythe.[15] The first one is based on unpublished experimental measurements performed in the (140 to 273) K temperature range. Its relative deviation from our empirical relation is lower than 4 %. The second one is based on experimental data acquired between (151.52 and 192.54) K. It deviates significantly from the data at temperatures lower than 140 K and higher than 240 K. The CSMGem code provides data only for temperatures higher than 240 K. In the (240 to 273) K temperature range, the equilibrium pressure computed with this code presents a slight relative deviation of ± 4 %, but the slope of this curve seems to be too large.

At low temperatures, the curve of the clathrate hydrate equilibrium intersects the sublimation curve of carbon dioxide solid. Thus, as for propane,[28] the carbon dioxide clathrate hydrate presents a quadruple point at which carbon dioxide clathrate hydrates, water ice, solid carbon dioxide, and gaseous carbon dioxide are at thermodynamic equilibrium. Miller and Smythe[15] and Longhi[29] find respectively a temperature of (121 and 135) K for this quadruple point. Using our empirical relation for CO_2 clathrate hydrate and the one of Fray and Schmitt[30] for carbon dioxide solid, we find that this quadruple point of carbon dioxide clathrate hydrate is located at $T = (132.4 \pm 0.8)$ K and $P = (5.0 \pm 0.8)\ 10^{-2}$ kPa. For temperatures below 132.4 K, a mixture of pure water and carbon dioxide solid is more stable than the carbon dioxide clathrate hydrate.

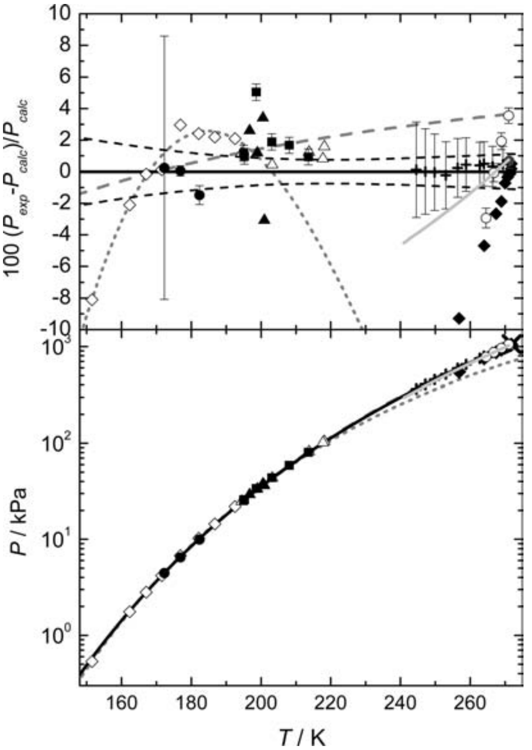

Figure 5. Equilibrium pressure of carbon dioxide clathrate hydrates as a function of the temperature for the HIV three-phase equilibrium (lower panel) and deviation of the experimental equilibrium pressures from those calculated by the empirical relation (upper panel): ●, this work; ×, Q1 quadruple point; ◆, Larson;[27] ◇, Miller and Smythe;[15] ▲, Adamson and Jones;[54] △, Falabella and Vanpee;[34] ■, Schmitt;[21] □, Wendland et al.;[33] +, Yasuda and Ohmura;[19] ○, Mohammadi and Richon;[20] solid black line, empirical relation determined in this work; dotted black line, confidence band at 95 % of our empirical relation; solid gray line, CSMGem prediction;[1] dashed gray line, empirical relation of Miller;[7] dotted gray line, empirical relation determined by Miller and Smythe.[15]

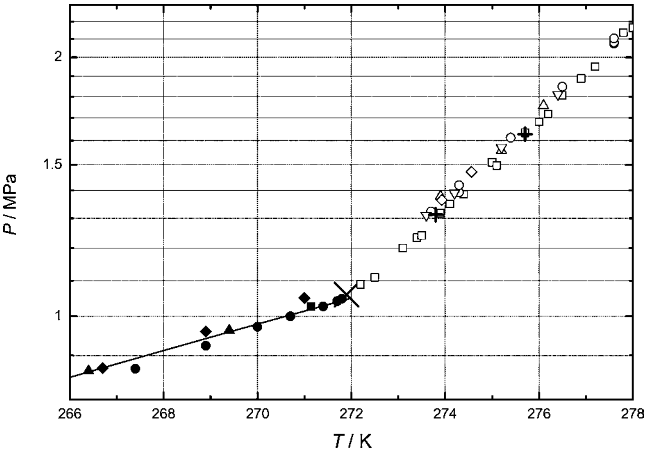

Figure 6. Equilibrium pressure of carbon dioxide clathrate hydrate as a function of the temperature for the HIV and HLV three-phase equilibria: ×, Q1 quadruple point determined in this study; ●, Larson;[27] ■, Wendland et al.;[33] ▲, Yasuda and Ohmura;[19] ♦, Mohammadi and Richon;[20] solid black line, empirical relation determined in this work for the HIV equilibrium; □, Larson;[27] ○, Deaton and Frost;[17] △, Robinson and Metha;[31] ▽, Fan and Guo;[32] ◇, Wendland et al.;[33] +, Yasuda and Ohmura.[19]

Considering the L_W−H−V equilibrium data measured by Larson,[27] Deaton and Frost,[17] Robinson and Metha,[31] Fan and Guo,[32] Wendland et al.,[33] and Yasuda and Ohmura,[19] we can determined that the Q1 quadruple point should be located at (271.9 ± 0.1) K and (1060 ± 20) kPa. This latter value is about

Table 4. Parameters of the Empirical Relations To Calculate the Equilibrium Pressure as a Function of the Temperature for the HIV Equilibrium of Simple Guest Clathrate Hydrates of Xenon, Carbon Dioxide, and Methane

	parameters of the empirical relation		temperature range of the experimental data (K)
compounds	*A*	*B*	
xenon	16.62	−3159	167.47 to 273.15
carbon dioxide	16.39	−2565	151.52 to 271.8
methane	15.78	−2176	82 to 272.2

200 kPa lower than the one published in Sloan and Koh.[1] Figure 6 shows the location of this quadruple point.

Clathrate Hydrate of Methane. Concerning methane clathrate hydrates, we have performed six measurements ranging from 145.75 K (2.4 kPa) to 195.74 K (103.2 kPa). These measurements are reported in Figure 7 and Table 3. The equilibrium pressures that we measured progressively diverge at low temperatures from the ones of Falabella and Vanpee[34] performed in the same temperature range. We find no reason to explain this deviation except possibly a constant positive bias of about 3 kPa in their data (four times their stated uncertainty). As the experimental data concerning the methane clathrate hydrate are quite dispersed, we take into account only our measurements as well as the ones of Delsemme and Wenger[35] and of Yasuda and Ohmura[19] to compute an empirical relation. This empirical relation reproduces the experimental measurements with a relative deviation of ± 10 %. The empirical relation previously used in astrophysical models is the one of Miller[7] which is based on unpublished results acquired over the (175 to 207) K temperature range. Its relative deviation from our first empirical relation is lower than 5 % between (80 and 270) K. On the contrary, the equilibrium pressures computed with the CSMGem code present a relative deviation reaching −35 % at 170 K. Furthermore, as for carbon dioxide, the slope of this curve seems to be too large.

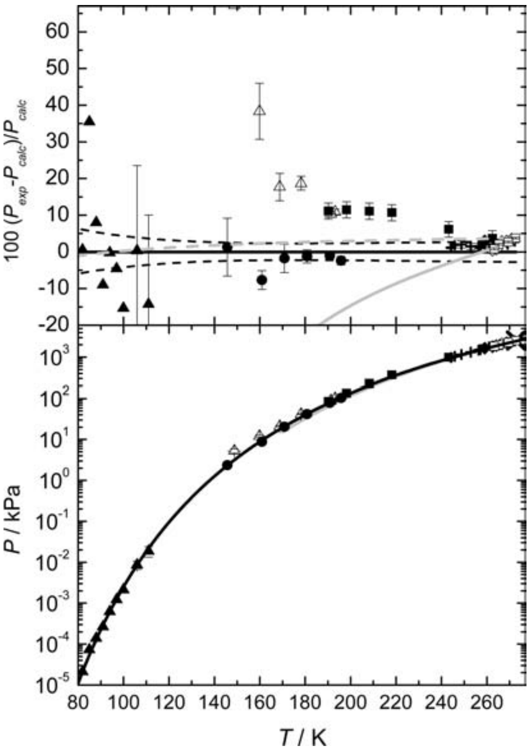

Figure 7. Equilibrium pressure of methane clathrate hydrates as a function of the temperature for the HIV equilibrium (lower panel) and deviation of the experimental equilibrium pressures from those calculated by the empirical relation (upper panel): ●, this work; ×, Q1 quadruple point; ◆, Roberts et al.;[55] ◇, Deaton and Frost;[17] ▲, Delsemme and Wenger;[35] △, Falabella and Vanpee;[34] ■, Makogon and Sloan;[56] +, Yasuda et al.;[19] □, Mohammadi and Richon;[57] solid black line, empirical relation determined in this work; dotted black lines, confidence band at 95 % of our empirical relation; solid gray line, CSMGem prediction;[1] dashed gray line, empirical relation determined by Miller.[7]

Considering the L_W−H−V equilibrium data measured by Deaton and Frost,[17] Snell et al.,[36] Jhaveri and Robinson,[37] De Roo et al.,[38] Adisasmito et al.,[39] Kang and Huen,[40] Nakamura et al.,[41] Ohmura et al.,[42] and Mohammadi et al.,[43] we can determine that the Q1 quadruple point should be located at (272.9 ± 0.2) K and (2540 ± 30) kPa. This latter value is in agreement with the one published by Sloan and Koh.[1]

Conclusion

We reported experimental I−H−V equilibrium data for xenon from (167.20 to 246.16) K, carbon dioxide from (172.28 to 182.15) K, and methane from (145.75 to 195.74) K. For xenon, we have shown that the data of Barrer and Edge[18] present a systematic deviation compared to our measurements and the ones of Makogon et al.[25] So far, the I−H−V equilibria for krypton and argon clathrate hydrates have only been measured by Barrer and Edge.[18] The discovery of the discrepancy for xenon casts some doubts on the validity of all of the measurements of these authors and therefore on the extrapolation law for krypton and xenon which are used in astrophysical models. For carbon dioxide, the different data sets present a very good agreement. Comparing the I−H−V equilibrium of carbon dioxide clathrate hydrate and the stability of carbon dioxide ice, we show that, for temperatures lower than (132.4 ± 0.8) K, a mixture of water and carbon dioxide ices should be thermodynamically more stable than carbon dioxide clathrate hydrate. For methane, the different data sets present a relative discrepancy reaching 70 %.

For these three molecular species, from our measurements as well as the ones already published in the literature, we derive empirical relations allowing us to calculate the equilibrium pressure of the clathrate phase at any temperature below the freezing point of water (see Table 4). Rigorously, these empirical relations have to be considered as interpolations in the temperature range of the experimental measurements. The validity of the extrapolations at very low temperatures, as the ones used in astrophysical models, could be questioned. Indeed, the empirical relation that we used derived from the Clausius−Clapeyron equation assumes that: (i) the molar volume of the condensed phase is negligible against that of gas, (ii) the gas is perfect, and (iii) the phase-change enthalpy is supposed to be independent of temperature. The first assumption is verified; nevertheless, the experimental measurements have been performed at pressures at which the perfect gas assumption is generally not verified, and the enthalpies of clathrate hydrate dissociation are known to vary at low temperatures.[44−46] Thus, the use of these empirical relations at very low temperatures has to be performed with caution. Moreover, these empirical relations are valid only for pure clathrate hydrates, whereas multiguest clathrate hydrates should be formed in an astrophysical environment. Unfortunately, there is a paucity of data concerning the composition and equilibrium of multiguest clathrate hydrates at temperatures below the freezing point of water. New measurements on the equilibrium of multiguest clathrate hydrates at low temperatures are welcome to constrain the partition of the considered molecules between the gaseous and the solid phases during the formation of these multiguest clathrate hydrates.

Concerning the possible formation and presence of clathrate hydrates in astrophysical objects, two issues remain unsolved: the kinetics of clathrate hydrates formation from water ice crystals at low temperature and the direct detection of clathrate hydrates on astrophysical and planetary objects. Indeed, for the moment, natural clathrate hydrates have only been found on Earth, and no clathrate hydrate has been detected on others astrophysical objects. Thus, some spectroscopic studies, such as the ones of Dartois et al.,[47−49] specifically devoted to the search of clathrate hydrates on astrophysical objects have to be performed.

As the kinetics of clathrate hydrates formation and decomposition is not well-understood, it is generally not taken into account in astrophysical models. Indeed, the pioneering studies of Barrer and Edge[18] at low temperatures have already revealed that the formation rate of clathrate hydrates do not depend only on the temperature and pressure but also of the nature of the ice crystals. Sloan[50] states that clathrate hydrate kinetics is the largest challenge to future understanding of clathrate hydrates. Nevertheless, different authors[21,51−53] have already revealed that the mobility and the diffusion of water molecules at the surface of the ice crystals is a critical parameter controlling the formation kinetics of clathrate hydrates at low temperatures. Quantitative studies on the formation of clathrate hydrates from ice crystals would be welcome to introduce such considerations in astrophysical models.

Acknowledgment

We acknowledge E. Dartois for helpful discussions concerning the formation at low temperature and the infrared spectroscopy of clathrate hydrates as well as D. Gautier, D. Bockelée-Morvan, O. Mousis, D. Prianik, and M. Podolak for encouragement and discussions about their astrophysical models.

Literature Cited

(1) Sloan, E. D.; Koh, C. *Clathrate hydrates of Natural Gases*, 3rd ed.; CRC Press, Taylor & Francis Group: Boca Raton, FL, 2007.

(2) Max, M. D. *Natural Gas Hydrate in Oceanic and Permafrost Environments*; Kluwer Academic Publishers: Dordrecht, Netherlands, 2000.

(3) Lunine, J. I.; Stevenson, D. J. Thermodynamics of clathrate hydrate at low and high pressures with application to the outer solar system. *Astrophys. J., Suppl. Ser.* **1985**, *58*, 493–531.

(4) Miller, S. L. *Solar System Ices*; Schmitt, B., De Bergh, C., Festou, M., Eds.; Kluwer Academin Publishers: Dordrecht, Netherlands, 1998; pp 59−79.

(5) Kargel, J. S.; Lunine, J. I. *Solar System Ices*; Schmitt, B., De Bergh, C., Festou, M., Eds.; Kluwer Academin Publishers: Dordrecht, Netherlands, 1998; pp 97−118.

(6) Delsemme, A. H.; Swings, P. Gas hydrates in cometary nuclei and interstellar grains. *Ann. Astrophys.* **1952**, *15*, 1–6.

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

(8) Lewis, J. S. Low temperature condensation from the solar nebula. *Icarus* **1972**, *16*, 241–252.

(9) Sill, G. T.; Wilkening, L. L. Ice clathrate as a possible source of the atmospheres of the terrestrial planets. *Icarus* **1978**, *33*, 13–22.

(10) 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.

(11) 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.

(12) 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.

(13) Osegovic, J. P.; Max, M. D. Compound clathrate hydrate on Titan's surface. *J. Geophys. Res., [Planets]* **2005**, *110*, 08004.

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

(15) Miller, S. L.; Smythe, W. D. Carbon Dioxide Clathrate in the Martian Ice Cap. *Science* **1970**, *170*, 531–533.

(16) Marboeuf, U.; Mousis, O.; Petit, J.-M.; Schmitt, B. Clathrate Hydrates Formation in Short-Period Comets. *Astrophys. J.* **2010**, *708*, 812–816.

(17) 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.

(18) 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.

(19) 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.

(20) Mohammadi, A. H.; Richon, D. Equilibrium Data of Nitrous Oxide and Carbon Dioxide Clathrate Hydrates. *J. Chem. Eng. Data* **2008**, *54*, 279–281.

(21) Schmitt, B. La surface de la glace: structure, dynamique et interactions - Implications astrophysique. Ph.D. Thesis, University of Grenoble, Grenoble, France, 1986.

(22) Moudrakovski, I. L.; Sanchez, A. A.; Ratcliffe, C. I.; Ripmeester, J. A. Nucleation and growth of hydrates on ice surfaces: New insights from Xe-129 NMR experiments with hyperpolarized xenon. *J. Phys. Chem. B* **2001**, *105*, 12338–12347.

(23) Yoon, J. H.; Kawamura, T.; Yamamoto, Y.; Komai, T. Transformation of methane hydrate to carbon dioxide hydrate: In situ Raman spectroscopic observations. *J. Phys. Chem. A* **2004**, *108*, 5057–5059.

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

(25) Makogon, T. Y.; Mehta, A. P.; Sloan, E. D. Structure H and Structure I Hydrate Equilibrium Data for 2,2-Dimethylbutane with Methane and Xenon. *J. Chem. Eng. Data* **1996**, *41*, 315–318.

(26) Thomas, C.; Mousis, O.; Ballenegger, V.; Picaud, S. Clathrate hydrates as a sink of noble gases in Titan's atmosphere. *Astron. Astrophys.* **2007**, *474*, L17–L20.

(27) Larson, S. D. Phase Studies of the Two Component Carbon Dioxide-Water System, Involving the Carbon Dioxide Hydrate. Ph.D. Thesis, University of Illinois, Urbana, IL, 1955 (quoted in ref 1).

(28) Harmens, A.; Sloan, E. D. The Phase-Behavior of the Propane Water-System - a Review. *Can. J. Chem. Eng.* **1990**, *68*, 151–158.

(29) Longhi, J. Phase equilibria in the system CO_2-H_2O I: New equilibrium relations at low temperatures. *Geochim. Cosmochim. Acta* **2005**, *69*, 529–539.

(30) Fray, N.; Schmitt, B. Sublimation of ices of astrophysical interest: A bibliographic review. *Planet. Space Sci.* **2009**, *57*, 2053–2080.

(31) Robinson, D. B.; Metha, B. R. Hydrates in the Propane-Carbon Dioxide-Water System. *J. Can. Pet. Technol.* **1971**, *10*, 33–35.

(32) Fan, S. S.; Guo, T. M. Hydrate Formation of CO_2-Rich Binary and Quaternary Gas Mixtures in Aqueous Sodium Chloride Solutions. *J. Chem. Eng. Data* **1999**, *44*, 829–832.

(33) Wendland, M.; Hasse, H.; Maurer, G. Experimental Pressure-Temperature Data on Three- and Four-Phase Equilibria of Fluid, Hydrate, and Ice Phases in the System Carbon Dioxide-Water. *J. Chem. Eng. Data* **1999**, *44*, 901–906.

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

(35) Delsemme, A. H.; Wenger, A. Physico-chemical phenomena in comets−I. Experimental study of snows in a cometary environment. *Planet. Space Sci.* **1970**, *18*, 709–715.

(36) Snell, L. E.; Otto, F. D.; Robinson, D. B. Hydrates in systems containing methane, ethylene, propylene, and water. *AIChE J.* **1961**, *7*, 482–485.

(37) Jhaveri, J.; Robinson, D. B. Hydrates in the Methane-Nitrogen System. *Can. J. Chem. Eng.* **1965**, *43*, 75–77.

(38) De Roo, J. L.; Peters, C. J.; Lichtenthaler, R. N.; Diepen, G. A. M. Occurrence of methane hydrate in saturated and unsaturated solutions of sodium chloride and water in dependence of temperature and pressure. *AIChE J.* **1983**, *29*, 651–657.

(39) Adisasmito, S.; Frank, R. J.; Sloan, E. D. Hydrates of carbon dioxide and methane mixtures. *J. Chem. Eng. Data* **1991**, *36*, 68–71.

(40) Kang, S.-P.; Huen, L. Clathrate phase equilibria for the water-phenol-methane system. *Fluid Phase Equilib.* **1998**, *146*, 339–349.

(41) Nakamura, T.; Makino, T.; Sugahara, T.; Ohgaki, K. Stability boundaries of gas hydrates helped by methane−structure-H hydrates of methylcyclohexane and cis-1,2-dimethylcyclohexane. *Chem. Eng. Sci.* **2003**, *58*, 269–273.

(42) Ohmura, R.; Uchida, T.; Takeya, S.; Nagao, J.; Minagawa, H.; Ebinuma, T.; Narita, H. Clathrate hydrate formation in (methane + water + methylcyclohexanone) systems: the first phase equilibrium data. *J. Chem. Thermodyn.* **2003**, *35*, 2045–2054.

(43) Mohammadi, A. H.; Anderson, R.; Tohidi, B. Carbon Monoxide Clathrate Hydrates: Equilibrium Data and Thermodynamic Modeling. *AIChE J.* **2005**, *51*, 2825–2833.

(44) 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.

(45) 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.

(46) Anderson, G. K. Enthalpy of dissociation and hydration number of methane hydrate from the Clapeyron equation. *J. Chem. Thermodyn.* **2004**, *36*, 1119–1127.

(47) Dartois, E.; Deboffle, D. Methane clathrate hydrate FTIR spectrum. Implications for its cometary and planetary detection. *Astron. Astrophys.* **2008**, *490*, L19–L22.

(48) Dartois, E.; Schmitt, B. Carbon dioxide clathrate hydrate FTIR spectrum. Near infrared combination modes for astrophysical remote detection. *Astron. Astrophys.* **2009**, *504*, 869–873.

(49) Dartois, E.; Deboffle, D.; Bouzit, M. Methane clathrate hydrate infrared spectrum - II. Near-infrared overtones, combination modes and cages assignments. *Astron. Astrophys.* **2010**, *515*, A49–A54.

(50) Sloan, E. D. Clathrate hydrate measurements: microscopic, mesoscopic, and macroscopic. *J. Chem. Thermodyn.* **2003**, *35*, 41–53.

(51) Price, P. B. Kinetics of Conversion of Air Bubbles to Air Hydrate Crystals in Antarctic Ice. *Science* **1995**, *267*, 1802–1804.

(52) Pietrass, T.; Gaede, H. C.; Bifone, A.; Pines, A.; Ripmeester, J. A. Monitoring Xenon Clathrate Hydrate Formation on Ice Surfaces with Optically Enhanced ^{129}Xe NMR. *J. Am. Chem. Soc.* **1995**, *117*, 7520–7525.

(53) Jin, Y.; Nagao, J.; Hayashi, J.; Shimada, W.; Ebinuma, T.; Narita, H. Observation of Xe Hydrate Growth at Gas-Ice Interface by Microfocus X-ray Computed Tomography. *J. Phys. Chem. C* **2008**, *112*, 17253–17256.

(54) Adamson, A. W.; Jones, B. R. Physical Adsorption of Vapors on Ice. IV. Carbon Dioxide. *J. Colloid Interface Sci.* **1971**, *37*, 831–835.

(55) 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.

(56) Makogon, T.; Sloan, J. E. Phase Equilibrium for Methane Hydrate from 190 to 262 K. *J. Chem. Eng. Data* **1995**, *40*, 344–344.

(57) 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.

(58) Falabella, B. J. A Study of Natural Gas Hydrates. Ph.D. Thesis, University of Massachusetts, Ann Arbor, MA, 1975 (quoted in ref 1).

Received for review June 17, 2010. Accepted September 9, 2010. N.F. thanks CNES for a postdoctoral fellowship. This work has been supported by the French “Centre National d’Etudes Spatiales” (CNES) and by the Research Network Program in Astrophysics from the The Israeli-French High Council for Science and Technology Research.

JE1006604