

# Cage Occupancy and Compressibility of Deuterated N<sub>2</sub>-Clathrate Hydrate by Neutron Diffraction

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**Abstract.** This paper reports pressure dependent high resolution neutron diffraction work on N<sub>2</sub>-clathrates, which for the first time provides numbers on the compressibility as well as the location and degree of filling of the guest molecules in the small and large cages. N<sub>2</sub>-clathrates crystallize, at least at lower pressures and temperatures near 0 °C, in the Stackelberg type II structure. However, during the diffraction experiments we have observed the transient and partial formation of the von Stackelberg type I N<sub>2</sub>-clathrate at pressures exceeding several hundred bar. The filling of the small cages in the type II clathrate roughly follows a Langmuir isotherm. In contrast to most previous assumptions there is strong evidence that the large cages are doubly occupied in both type I and type II N<sub>2</sub>-clathrates. The observed filling can be fitted reasonably well by a two-constant Langmuir model.

**Key words:** Clathrate hydrate, Langmuir isotherm, cage occupancy, neutron diffraction, compressibility.

## 1. Introduction

The work presented in this paper was undertaken in the context of the study of natural air clathrates in polar ice sheets. Several aspects of the processes leading to the inclusion of air in ice and to the eventual formation of air hydrate clathrates need further investigation. We have focused our attention on the relative concentration of nitrogen and oxygen as the main constituents of the atmosphere occluded in the clathrates, on the depth profile of the clathrate number, size and shape distribution, and the molecular degree of filling of the air constituents in the clathrate phase.

The isotopic and chemical composition of the trapped air and of the surrounding ice is one of the most precise palaeoclimatic indicators [1]. Air bubbles in ice transform at approximately 800–1300 m into air clathrates, depending on the tem-

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perature of the ice [2]. Yet the interpretation of the air inclusions is hampered by this transformation as their composition is not necessarily representative of the air from which the clathrates most probably form. For the reconstruction of palaeoatmospheres, information on the composition and the amount of the air included in the clathrates is desirable. To obtain information on the composition of the air enclosed in the clathrates we carried out a series of Raman spectroscopic studies [3–5]. The depth profile of clathrate distribution in polar ice cores is correlated with climatic factors. This has been shown in an investigation on the Vostok ice core [6] and in a preliminary study on the GRIP ice core [5]. To determine the amount of air in the clathrates (from the molecular occupancy in the clathrate cages) and to elucidate their physicochemical properties we have started neutron diffraction work on synthetic samples of N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and CH<sub>4</sub> clathrates. Results on a series of N<sub>2</sub> clathrates in the pressure range between 150 and 2500 bar will be presented here.

The first Raman spectroscopic studies on natural ice clathrates from the Dye-3 deep ice core showed a molecular nitrogen/oxygen ratio of 1.7 (atmospheric value: 3.7), implying strong fractionation [7]. In a more extensive study it could be shown that the average N<sub>2</sub>/O<sub>2</sub> ratio in clathrates is in closer agreement with the overall gas content and the present atmospheric ratio: integration of the N<sub>2</sub> and O<sub>2</sub> Raman intensities in the combined spectrum of 144 specimens from 21 different depths in the **GR**eenland **I**ce **C**ore **P**roject (GRIP) deep ice core yielded a ratio of 3.51, with an average of 3.6 (esd: 0.4) calculated from the individual spectra [3].

The different dissociation pressures of nitrogen clathrate (160 bar) and oxygen clathrate (120 bar) at 0 °C [8, 9] could imply clathrate formation of these species at different depth levels. As clathrate formation starts at the ice matrix/air bubble boundary [10] and the pressure requirement for oxygen clathrate is met before that for nitrogen clathrate, the result might be a concentration gradient from a higher oxygen concentration at the clathrate margin to a higher nitrogen concentration in the clathrate centre. However, Raman spectroscopic scans to determine the N<sub>2</sub>/O<sub>2</sub> ratios on different planes through a clathrate, with the two scan axes perpendicular to one another, do not point to a very non-uniform gas distribution in clathrates [4].

We investigated the possibility of fractional decomposition on core relaxation due to the higher dissociation pressure of nitrogen clathrate. The N<sub>2</sub>/O<sub>2</sub> ratios in different positions on a decomposing clathrate specimen, ranging from pure clathrate to pure air bubble, do not point to different retransformation rates between oxygen and nitrogen. The N<sub>2</sub>/O<sub>2</sub> ratio is essentially retained in the resulting secondary air bubbles [4]. However, initial fractionation and concentration gradients may have been levelled out by either the dynamic behaviour of the matrix ice or recrystallization of the clathrate lattice and subsequent exchange of the occluded gases. Co-clathration of N<sub>2</sub> and O<sub>2</sub> at all stages of clathrate formation is also conceivable. N<sub>2</sub> and O<sub>2</sub> have only slightly different shapes of their van der Waals surfaces and may be incorporated into the small and the large cages in the clathrate lattice in different proportions.

To answer the question of whether the air is completely occluded in clathrates or whether a certain proportion is dissolved or diffused in the ice matrix it is necessary to determine the amount of air in clathrates from an estimate of the clathrate/ice volume ratio. By calculating the amount of air per unit volume of clathrate, the air/ice ratio can be inferred. As clathrates are non-stoichiometric compounds, it is necessary to know the degree of filling of the molecules in the clathrate cages, which in turn is a function of the pressure of the overburden ice.

Natural air clathrates as present in deeper parts of the Arctic and Antarctic ice sheets [11], e.g. in the GRIP or Dye-3 (Greenland) and Vostok (Antarctica) deep ice cores, crystallize in the von Stackelberg type II structure, as shown by an X-ray study on clathrates from the Dye-3 ice core [12]. The existence of two main types of clathrate hydrate structures was reported by von Stackelberg [13,14]. In both structures, the H<sub>2</sub>O molecules form a lattice consisting of cage-like arrangements of two different sizes, which can accommodate individual guest molecules. Their cubic structures differ in the size of the unit cell (type I: ca. 12 Å, type II: ca. 17 Å) and in the size of the cages. Type I forms two 12-hedral and six 14-hedral cages per unit cell, whereas sixteen 12-hedral and eight 16-hedral cages are present in structure II. It was generally believed that small guest molecules (van der Waals diameter less than 5.9 Å) give rise to the formation of structure I, while larger molecules (van der Waals diameter between 5.9 and 6.9 Å) lead to a type II structure [14], but more recent investigations have shown that very small molecules (N<sub>2</sub>, O<sub>2</sub>, Ar, Kr) are also accommodated in a type II structure [15–18]. The ratio of medium-sized and small cages in structure I is 3, whereas that of large and small cages in structure II is 0.5. In the type II structure the bonding parameters of the H<sub>2</sub>O molecules are more similar to those of hexagonal ice as compared to type I, which leads to an intrinsically greater stability of type II structures [15].

To understand the formation of air clathrates as multicomponent compounds, a detailed knowledge of clathrate thermodynamics of the individual components of the atmosphere is crucial. In order to obtain information on the pressure dependency of the occupancy of the individual gas molecules in both cages in the two clathrate structures, we have started to prepare synthetic clathrates of nitrogen, oxygen, argon, carbon dioxide, and methane. In this work, we present an isothermic series ( $T = 273$  K) of nitrogen clathrates synthesized in a pressure range from 150 to 2500 bar and investigated by neutron diffraction techniques. The phase diagram of the N<sub>2</sub> – water system is shown in Figure 1.

## 2. Experimental

### 2.1. NEUTRON DIFFRACTION

Any *in-situ* work on air, N<sub>2</sub> or O<sub>2</sub> clathrates faces the experimental problem of maintaining pressures exceeding 100 bar during the investigation. Even if clathrates are metastable at ambient pressures (at least at lower temperatures), a determination of the equilibrium properties (e.g. expansivities, compressibilities and filling) can

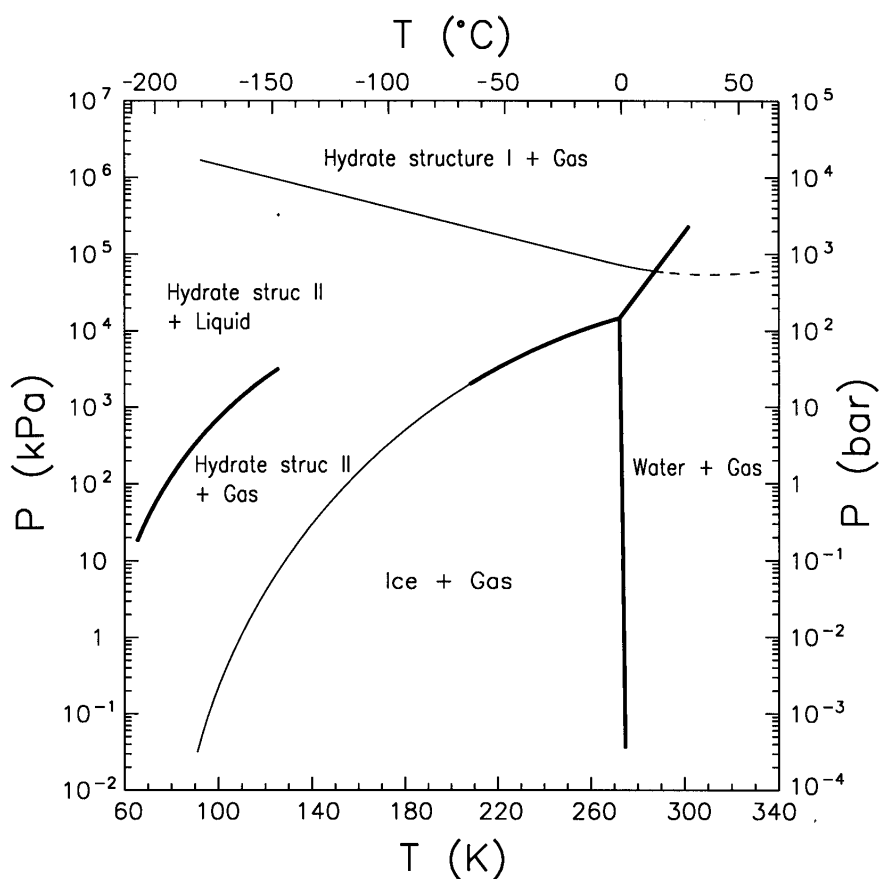


Figure 1. Phase diagram of N<sub>2</sub> clathrate. The thick lines are established by experiment. The thin lines are either calculated or extrapolated phase boundaries. The experimental clathrate-ice and clathrate-water boundaries are compiled from published work [8, 9, 19]. The theoretical boundary between a type I and type II structure was taken from Ref. [20].

be done only at controlled elevated pressures. Standard X-ray diffraction techniques are not suitable for this purpose as cells for elevated gas pressures in the 10<sup>2</sup>–10<sup>3</sup> bar range exhibit too much absorption for high precision work. Fortunately, this problem can be overcome by using high resolution neutron diffraction techniques. Quite a few convenient pressure cell materials (Al, Ti–Zr alloys) have low linear absorption coefficients for neutrons such that bulky high pressure cells for work up to gas pressures of at least 6 kbar can be used almost routinely. In addition, neutrons provide excellent information on the location of H or D atoms, which X-rays cannot give. A slight disadvantage is the high incoherent scattering cross section of hydrogen, which leads to sample absorption and high background for hydrogenated materials. Thus, deuterated samples are frequently used for neutron powder diffraction. One of us (WFK) had earlier started a project on high pressure

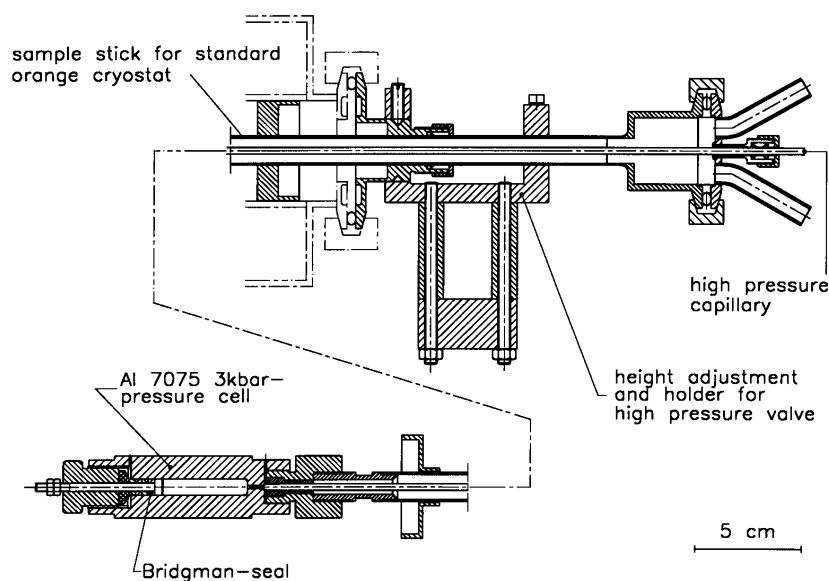


Figure 2. The MKI gas pressure cell for neutron scattering and its cryostat sample stick.

variable temperature neutron diffraction work on clathrate hydrates [18], which now comprises Ar, Kr, Xe, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> as guest species, among others. Here we report on the first results obtained in the N<sub>2</sub>-D<sub>2</sub>O system.

## 2.2. SAMPLE PREPARATION

*In-situ* formation of clathrate hydrates on the neutron diffractometer proved impractical as the formation kinetics are usually too slow to make efficient use of the beam time granted. Thus we had to develop and construct a set of neutron gas pressure cells (shown in Figure 2) for off-beam sample preparation and ready insertion into standard neutron variable temperature cryostats. A gas handling and mixing system has been set up for sample preparation and physicochemical work at the MKI Göttingen.

To provide a large reaction surface typically 1 g of D<sub>2</sub>O ice Ih is finely powdered in a glove box under dry nitrogen gas (to avoid isotopic exchange of the sample with H<sub>2</sub>O); the typical particle size of the crystallites is initially 15 μm (however, some grain growth is likely to take place in the course of the experiment before the completion of the clathrate formation). The powder is inserted in a pressure cell kept at dry ice temperatures. The cell is then transferred to the gas handling system and checked for leakages at pressures below the onset of the clathrate formation. After tightening up the different seals the pressure cell is equilibrated at the temperature of the sample preparation, usually at 0 °C. Subsequently, the gas pressure is raised in a few seconds to the value at which the formation is to take place. The pressure losses due to the uptake of the gas on clathration are

compensated manually; by this action the pressure is kept in a narrow range around the target value with mean deviations of typically 2–3 bar. The clathrate formation rates for N<sub>2</sub> were higher in the initial stages and became very slow after several days. For preparations in the range of a few hundred bar roughly half of the sample transformed within a day; the transformation of the other half took much longer and usually some untransformed ice Ih was left, even after several weeks of reaction. This is attributed to the increasingly difficult access of the gas to untransformed ice Ih. However, it can be assumed that the fugacity of N<sub>2</sub> gas was identical (within the limit of the pressure variations given above) over the whole time of the transformation at the growth interface. Thus the cage filling supposedly took place under true equilibrium conditions. It should be mentioned that clathrate synthesis without tight pressure control leads to inhomogeneous fillings, as evidenced by our initial neutron diffraction work and discussed below. Such inhomogeneous samples may, however, be equilibrated by leaving the sample for several weeks to several months at a controlled pressure and temperature to allow for re-growth processes. All samples were checked after the neutron experiments for filling homogeneity by decomposing the clathrate under a closely controlled temperature increase with a concomitant observation of the pressure changes. Inhomogeneous samples will decompose over a wider range of temperatures (and indeed do when they are deliberately prepared in inequilibrium), while an equilibrated sample will decompose sharply at one temperature. The remaining water in the cell was recovered for an accurate measurement of the density, which allowed the D/H exchange to be determined using a capillary resonance technique. Some samples at higher pressure were prepared starting from silica wool wetted with approximately 1 g of D<sub>2</sub>O. This was done to avoid bulk melting of powdered ice Ih on pressure increase with much lower clathrate formation rates as a result. The data obtained were of the same quality for both preparation procedures described. Samples were kept at the preparation temperature typically for several weeks before the neutron experiment was undertaken; they were transported at the same temperature to the neutron facility. The maximum temperature variation during the whole period is estimated to be less than 0.5 °C for all preparations at 0 °C. The preparations at 295 K have a larger variation, in the order of 1–2 °C.

### 2.3. DATA COLLECTION AND ANALYSIS

All neutron diffraction experiments presented here were performed on the high-resolution powder diffractometer D2B at the high-flux reactor of the Institut Laue-Langevin in Grenoble. The diffractometer was operated in the high-flux mode with a typical  $\Delta d/d$  resolution of  $10^{-3}$ . The pressure cell connected to its sample holder was inserted into the D2B He-flow cryostat preset to the temperature of the sample. After initial adjustment of the beam definers to reduce the scattering from the pressure cell and to cut off the scattering from the Bridgeman seal of the cell, data

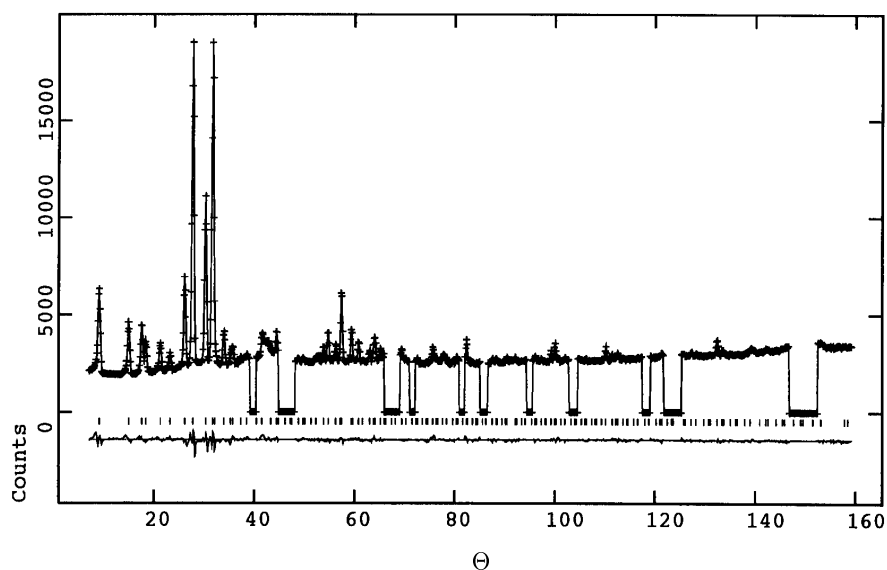


Figure 3. Neutron diffractogram of type II N<sub>2</sub> clathrate at 523 bar and 0 °C (counts vs. scattering angle). The bottom line denotes the differences between the observed and calculated intensities. Regions with zero intensity are excluded from the analysis due to the presence of Bragg reflections from the Al pressure cell.

were taken for 12–16 h for each sample to obtain a powder pattern in a scattering angle range of 5 to 160 °C at a wavelength in the vicinity of 1.59 Å.

The diffraction data were analysed and structure refinements were performed with the program GSAS [21]. Crystallographic least-squares structure refinement yields the lattice constants, the positional and thermal parameters, and the guest occupancies for each crystalline phase present in the sample. Instrumental and background parameters are determined together with the structural model parameters, a scale factor and the phase fractions in a full pattern refinement procedure ('Rietveld' refinement, see e.g. Ref. [22]). The estimated standard deviations derived in the least-squares procedure thus partly also reflect instrumental and sample imperfections, but not necessarily other systematic errors. Preferred orientation is a problem frequently encountered in powder diffraction; however, in this case the clathrate samples did not show any sign of deviation from an ideal powder, while the untransformed ice Ih powder remaining in the sample frequently showed considerable preferred orientation, an effect which was parameterized and accounted for in the least-squares refinement. A typical complete powder diffraction pattern obtained is shown in Figure 3. Some of the samples contained mixtures of type I and type II clathrates as shown in Figure 4, a fact which will be discussed below.

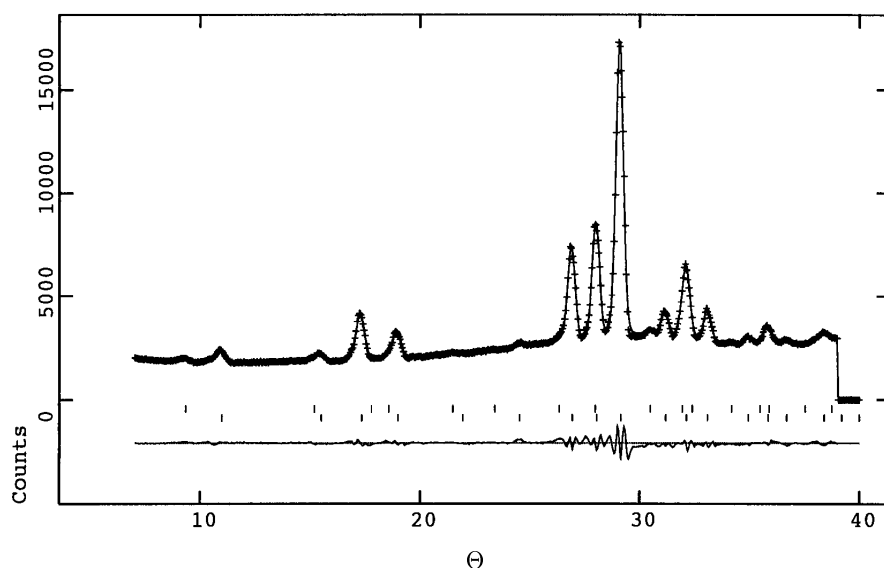


Figure 4. Low-angle neutron diffractogram of type I  $N_2$  clathrate at 1311 bar and  $0^\circ C$  (counts vs. scattering angle). Roughly 5% type II  $N_2$  clathrate is present. The top row of markers corresponds to type II, the bottom row of markers to type I reflection positions. The bottom line denotes the differences between the observed and calculated intensities.

### 3. Results

#### 3.1. LATTICE CONSTANTS AND COMPRESSIBILITIES

In a first series of experiments we obtained structural data for samples prepared at  $N_2$  pressures of 449, 578, 746, 1311 and 2427 bar. In this first series the pressure control was not as close as in later experiments with pressure variations of typically 5%; the term 'non-equilibrium' preparation will be attributed to these samples. The lattice constants obtained from the profile refinement for the type I and type II structure are given in Figure 5.

The volume compressibilities are obtained as the volume normalized pressure derivatives of the unit cell volume  $a_0^3$ ; the corresponding bulk modulus for type I  $N_2$  clathrate determined between 0.5 and 2.5 kbar gas pressure varies between 25 kbar and 42 kbar, respectively. These values are unusually low and may be attributed to the fact that the non-equilibrium filling was inhomogeneous and incomplete. The bulk modulus for type II  $N_2$  clathrate is almost constant over the pressure range investigated and amounts to 115 kbar; this is slightly higher than the corresponding bulk modulus of ice Ih.

#### 3.2. FILLING OF SMALL AND LARGE CAGES

In order to determine accurate values of the filling from crystallographic data the correct structural model for the location and orientation of the  $N_2$  molecule has



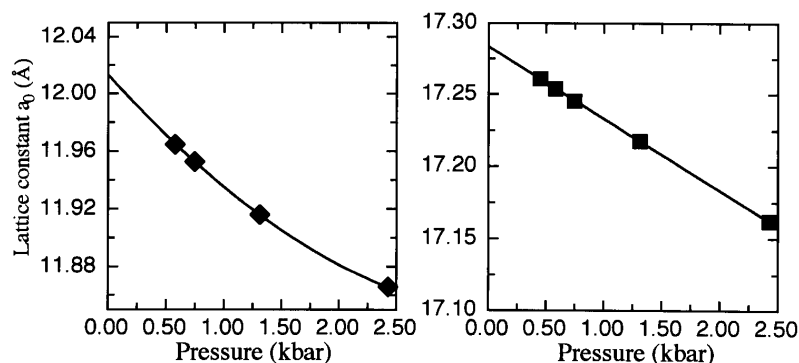


Figure 5. Lattice constants of type I (left) and type II (right)  $N_2$  clathrate vs. pressure at  $0^\circ\text{C}$ . The estimated standard deviation is less than the symbols given. The curve shown is a fitted polynomial function.

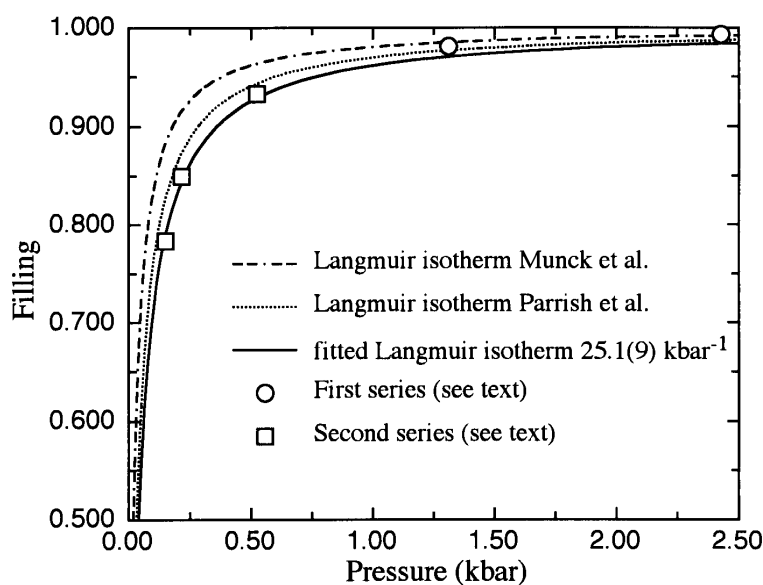


Figure 6. Comparison between the experimentally determined fillings of the small cages and theoretical calculations for  $N_2$  clathrate type II at  $0^\circ\text{C}$ . The experimental errors of the filling are in the order of 0.01, i.e. smaller than the symbol size. The fitted curve was calculated using only entries from the second series.

to be established first. This was done in two different ways: in a Monte-Carlo simulation using the CERIU<sup>2</sup> suite of programs, applying a universal force field, and imposing the crystallographically established host lattice geometry, the most frequently encountered molecular configurations were determined first. In a second step several compatible crystallographic models were refined and screened using convergence behaviour and crystallographic agreement factors as selection criteria.

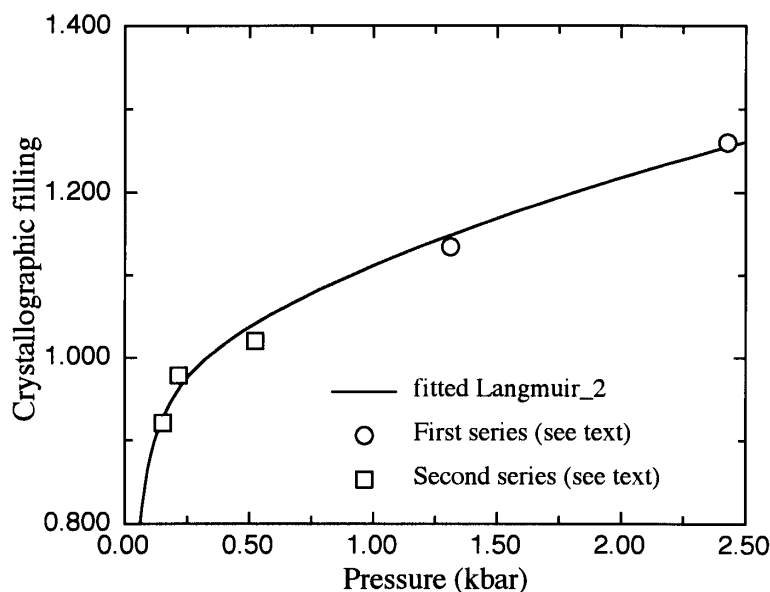


Figure 7. Filling of the large cages in N<sub>2</sub> clathrate type II at 0 °C. The experimental errors of the filling are in the order of 0.015, i.e. less than the symbol size. The fitted curve obtained from the two constant solid solution model is also shown (see text).

The best model for the small cage was locating the N<sub>2</sub> molecules at the cage centre with the molecular axis pointing along the cubic main axes for both the type I and type II structure. The best model for the large cage was locating the N<sub>2</sub> molecule shifted off the cage centre by approximately 0.8 Å with the molecular axes oriented parallel to the unit cell diagonals. Several other models have been tried, and it is noteworthy that these other models produce significant changes in the thermal motion parameters but only marginal changes in the cage occupancies. The final weighted profile *R*-factors were in all cases in the order of 0.02 to 0.03, which indicates excellent agreement between calculated and observed intensities.

In the first series of experiments we have determined the change of filling with time during the equilibration of samples prepared in non-equilibrium. This was done by repeated data collections after longer periods of equilibration extending up to 9 months. The main result is that in a fine powder at a temperature of 0 °C with several percent over- or underfilling the equilibrium composition is usually reached on a timescale of several weeks rather than days.

A second series of experiments was devoted to the determination of the filling of the small and large cages as a function of N<sub>2</sub> pressure under equilibrium conditions largely in the glaciologically relevant lower pressure range. For the type II structure the filling was determined for 0 °C at 155 bar (close to the decomposition pressure of 147 bar for deuterated N<sub>2</sub> clathrate) and at 523 bar. The filling of the small cage roughly follows a Langmuir isotherm and is thus to a first approximation

consistent with a solid solution model. This is to our knowledge the first time that the individual fillings of small and large cages have been determined experimentally under controlled  $p$ - $T$  conditions without any further physicochemical assumptions. These results may be compared with the calculations by Parrish and Prausnitz [23] and Munck *et al.* [24]; a better agreement is obtained with the former calculation, as shown in Figure 4. However, there is a significant deviation of our experimental data from a simple one-parameter Langmuir behaviour with relatively higher fillings at higher pressure. Note that the fitted Langmuir constant of  $25.1(9)$   $\text{kbar}^{-1}$  was obtained using only the data of our second experimental series. Coming first as a surprise but now corroborated by us in all structure refinements, is the fact that the large cages for all but the lowest pressures are partly doubly occupied. Consequently the abovementioned theoretical calculations are meaningless for the large cages as they were all carried out under the now unjustified assumption of single maximum occupancy. Figure 5 shows the filling of the large cages of structure type II as a function of pressure as well as a fit with a modified solid solution model allowing for double occupancy [25]. For cages with partial double occupancy two distinct Langmuir constants have to be introduced, one for single occupancy,  $C_A$  and another for double occupancy,  $C_{AA}$ . The filling fraction of singly occupied cages then is given by

$$y_A = C_{AP_A} / (1 + C_{AP_A} + C_A C_{AA} p_A^2),$$

while the filling fraction of doubly occupied cages is given by

$$y_{AA} = C_{AAP_A} y_A.$$

The crystallographically determined cage filling is the space average over all equivalent cages in the sample; consequently the crystallographic filling is related to  $y_A$  and  $y_{AA}$  by

$$y_{\text{crystallographic}} = y_A + 2y_{AA}.$$

From the measured values of  $y_{\text{crystallographic}}$  the following two Langmuir constants (at  $0^\circ\text{C}$ ) were obtained:  $C_A = 62.9(11.7)$   $\text{kbar}^{-1}$  and  $C_{AA} = 0.145(0.014)$   $\text{kbar}^{-1}$  with the least-squares estimated errors quoted in brackets. More data are needed to confirm the general validity of the model.

### 3.3. $\text{N}_2$ CLATHRATE WITH TYPE I STRUCTURE

In the first series of sample preparations massive surface melting of the powder grains is likely to have occurred and the formation of type I  $\text{N}_2$  clathrate may be partly attributed to the presence of liquid as later sample preparations using the silica wool technique and liquid water (see Section 2.2.) also produced mixtures of the type I and type II phase. An *in-situ* neutron diffraction run revealed that type

I is formed only in the initial stage of the experiment immediately after reaching the stability field of the N<sub>2</sub> clathrate. It appears that type I nucleates more readily than type II N<sub>2</sub> clathrate. However, the type I structure was not thermodynamically stable at any of the pressure investigated; the phase transformed completely into the type II clathrate over periods of several weeks to several months. This is also true for high pressures and temperatures (e.g. 295 K and 2427 bar) in a range where the type I structure was predicted to be the equilibrium form; the position of one of the predicted phase boundaries as given by Lundgaard and Mollerup [20] is shown above in Figure 1. From the observed transformation rates, however, we have some indication that despite a higher molecular mobility the transformation rates are lower at higher temperatures. Clearly we observe that the lower the pressure, the higher will be the transformation rate. As an example we quote the 578 bar run: 28.02% type I as measured at 0 °C, 18.99% 2 days later after cooling to 80 K and 6.10% at 0 °C 8 weeks later. A pressure dependent analysis of the filling for type I N<sub>2</sub> clathrate cannot yet be given due to the lack of data (the sometimes very small fraction of type I in the presence of type II causes fairly large errors in the refined filling fractions). Nevertheless, we may state that the large cages in type I structure are also undoubtedly partly doubly occupied.

#### 4. Conclusion

Neutron diffraction has proved to be an extremely useful technique for the investigation of clathrate hydrates. It allows one to establish the guest occupancies of the cages together with the host structure as a function of  $p$  and  $T$ . Thus, it is a unique tool to check the validity of different thermodynamic models of enclathration. From the results presented here it becomes clear that all previous calculations on N<sub>2</sub> clathrate have to be revised in order to explicitly include a double occupancy of the large cages. A similar double occupancy may also be expected in at least the O<sub>2</sub> and Ar clathrates. To prove this and to reveal details of the structural changes (filling and anisotropy of the cages, change of H bond length) on pressure variation, further neutron diffraction work is in progress.

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