

## DIFFUSION COEFFICIENT AND SOLUBILITY MEASUREMENTS OF NOBLE GASES IN ICE CRYSTALS

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**Abstract:** Diffusion coefficients and solubility of helium, neon and argon gases in ice crystals were determined by measuring the pressure rise in a vessel caused by gas emission from an ice sample supersaturated with the gas. Diffusion coefficients of helium, neon and argon gases in the temperature range between 258.2 K and 268.2 K were on the order of  $10^{-9}$  m<sup>2</sup> s<sup>-1</sup>,  $10^{-10}$  m<sup>2</sup> s<sup>-1</sup> and  $10^{-11}$  m<sup>2</sup> s<sup>-1</sup>, respectively. Solubilities of helium and neon gases in the molar fraction deduced from the total amount of emitted gases were on the order of  $10^{-6}$  and  $10^{-7}$ , respectively. As the diffusion coefficients of noble gases were found to depend on their molecular radii, the diffusion coefficients of air molecules, such as nitrogen and oxygen, in ice were estimated.

### 1. Introduction

When snow or firn transforms into ice at shallow depths of polar ice sheets, atmospheric air is captured in ice as air bubbles. However, air bubbles transform into air-hydrate crystals below a certain depth due to high pressure and low temperature. Since air components included in ice at deep depths must be the same as those in shallow ice, most air molecules are considered to be located in air-hydrate crystals.

The microscopic observation of air-hydrate crystals in Vostok ice cores, Antarctica, predicted the diffusion of air molecules in ice when air-hydrate crystals grow in ice (UCHIDA *et al.*, 1994). Furthermore, the solubility of air molecules in a deep ice sheet is also considered to become large due to the high hydrostatic pressure. If the diffusion rate or solubility of air molecules in ice is high, the air composition may change during the ice-core storage. Then serious problems must occur in the study of air components of the ancient atmosphere in ice cores.

Therefore, we should determine the diffusion rate and solubility of air-component molecules in ice. However, the diffusion coefficient of nitrogen molecules, which is a dominant component of the present atmosphere, was predicted to be too small to measure directly (SATOH *et al.*, 1994; UCHIDA *et al.*, 1994). Therefore, in the present study, we measured the diffusion coefficients and solubility of noble gases, such as helium,

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neon and argon by a method similar to that of SATOH *et al.* (1994). This method can measure both the diffusion coefficient and the solubility simultaneously. As the diffusion coefficient of helium gas has been measured by HAAS *et al.* (1971), we can check the performance of our experimental apparatus. However, there are only a few reports of diffusion coefficients of neon and argon in ice crystals.

The results indicated that the diffusion coefficient of gas molecules in ice crystals depends on the molecular size. (Hereafter, we use the word “molecule” for helium, neon and argon for the convenience.) Then we discuss the diffusion coefficients of nitrogen and oxygen molecules in ice.

## 2. Experimental Procedures

### 2.1. Experimental apparatus

Figure 1 shows a schematic diagram of the experimental apparatus. The apparatus is basically the same as that reported in a previous paper (SATOH *et al.*, 1994), but with some improvements in temperature control and in pressure measurement.

Both the reaction vessel and the reference vessel were made from SUS316 stainless steel to keep gas under high pressure (up to 15 MPa) without leakage for several weeks. A cylindrical ice sample (diameter  $d$  about 40 mm and height  $h$  about 29 mm) was set in the reaction vessel, and a cylindrical stainless-steel block of the same size as that of the

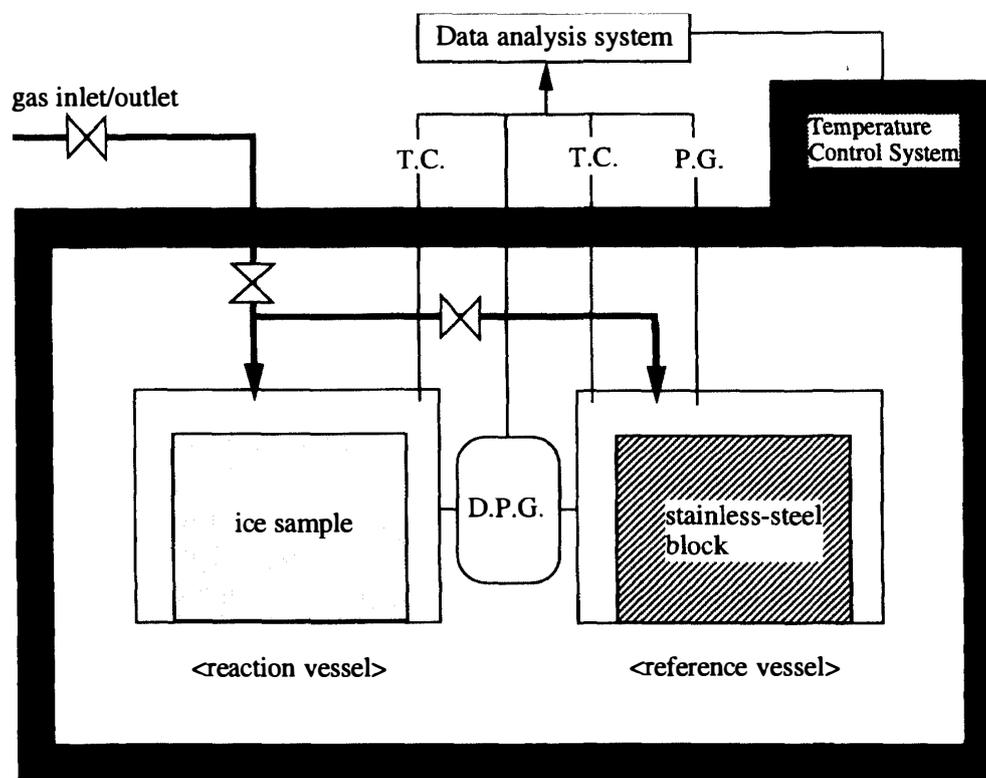


Fig. 1. Schematic diagram of experimental apparatus. D.P.G.: differential pressure gauge, T.C.: thermocouple, P.G.: pressure gauge.

ice sample was in the reference vessel. These two vessels were connected to a differential pressure gage (T.M. P21AA).

Figure 2 represents the schematic diagram of pressure  $P$  changes with time  $t$ . After a sample gas was introduced into both vessels at pressure  $P=P_0$  at  $t=t_0$ , the diffusion of gas molecules into the ice sample caused a small pressure drop in the reaction vessel, which finally reached equilibrium,  $P=P_1$  at  $t=t_1$ . Then the pressurized gas was released to the atmosphere. In that situation, the molecular concentration of the sample gas in the ice sample was oversaturated. Therefore, gas molecules diffuse out from the ice sample, and the pressure rises gradually to equilibrium,  $P=P_2$ , in the reaction vessel. The quantity  $P_2$  is similar to  $P_0-P_1$ , which is less than 0.1 MPa. This small pressure rise was measured as the pressure difference between the reaction vessel and the reference vessel by the differential pressure gauge. The  $P-t$  curve provides the diffusion coefficient  $D$  of the gas molecule from the ice sample as shown in the following section. The final pressure difference  $P_2$  represents the solubility of the gas molecules in ice under the experimental conditions.

We used two different ice samples. One is natural single crystal ice obtained from Mendenhall glacier and the other is artificial polycrystal ice made from distilled and deionized water. As sample gases, we used commercial helium, neon and argon (Hoxan Gas Co.), each of which has purity of more than 99%.  $P_0$  was approximately 7 MPa and the temperature range was between 258 and 268 K, controlled within 0.2 K by soaking the whole apparatus in a liquid bath of antifreeze.

## 2.2. Principle of calculations of the diffusion coefficient and solubility

As shown in Fig. 2, the pressure increases gradually with time from  $t_1$  to  $t_2$ . The

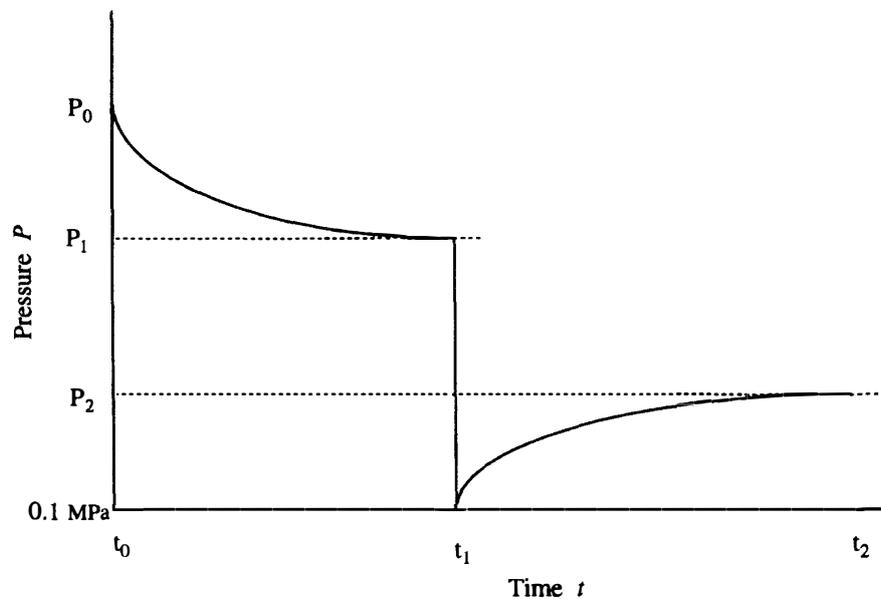


Fig. 2. Schematic diagram of pressure  $P$  change with time  $t$ . At  $t=t_0$ , a sample gas introduced was into vessels at  $P=P_0$ , then after  $P$  reached the equilibrium pressure  $P_1$  at  $t=t_1$ , the sample gas was released to the atmosphere.

pressure rise due to the physical desorption of gas molecules on the ice sample finished immediately after the gas release, which was considered to be smaller than the experimental error. The quantity of gas dissolved in the ice sample,  $Q$ , is denoted by the following differential equation written in cylindrical coordinates (HAAS *et al.*, 1971);

$$\frac{\partial Q}{\partial t} = D \left( \frac{\partial^2 Q}{\partial r^2} + \frac{1}{r} \frac{\partial Q}{\partial r} + \frac{\partial^2 Q}{\partial z^2} \right), \quad (1)$$

where  $D$  is the diffusion coefficient,  $r$  is the radial distance from the center of the cylinder and  $z$  is the longitudinal axis. The initial condition is  $Q=Q_1$  at  $t=t_1$ , where  $Q_1$  is the equilibrium gas quantity at pressure  $P=P_1$ . Since the ice sample is cylindrical, the boundary condition is  $Q=0$  at  $r \geq d/2$ . If we consider the quantity of gas molecules dissolved homogeneously at time  $t$  in the ice sample, the pressure  $P(t)$  at  $t=t$  is expressed by the following equation (CRANK, 1975):

$$\frac{P_2 - P(t)}{P_2} = \sum_{m=1}^{\infty} \sum_{n=1}^{\infty} \frac{2}{P_m} \frac{4}{\mu_n} \exp \left[ - \left[ \left( P_m \frac{2}{h} \right)^2 + \left( \frac{2\mu_n}{d} \right)^2 \right] Dt \right], \quad (2)$$

where  $p_m = (2m-1)\pi/2$ , and  $\mu_n$  is the  $n$ th solution of Bessel's equation. The experimental data were fitted to eq. (2) to obtain the value of  $D$  until the third term for helium and until the fifth term for both neon and argon. Because the pressure fluctuation due to the temperature fluctuation was rather large for about two hours after the gas release on our experimental apparatus, we fitted eq. (2) to data more than two hours after the gas release. Although eqs. (1) and (2) apply to the  $P$ - $t$  curve between  $t=t_0$  and  $t_1$ , we do not discuss this here because the results include large experimental errors.

Solubility of gas molecules in an ice sample is calculated from  $P_2$ . At  $t=t_1$ , the quantity of gas molecules is in equilibrium at  $P=P_1$ , but it is oversaturated at  $P=0.1$  MPa. Then the oversaturated gas starts to diffuse out from the ice sample. Finally, the quantity of gas molecules in ice samples reaches equilibrium at  $P=P_2$ . The amount of gas molecules calculated from  $P_2$  represents the quantity dissolved in ice samples at  $P=P_1$ . Although the solubility can be determined from  $P_0-P_1$ , it may include experimental errors such as gas leakage.

### 3. Results

The diffusion coefficient and solubility of noble gases in both single crystal and polycrystal ice samples were examined. Figure 3 shows the temperature dependence of the diffusion coefficients of helium ( $D_{\text{He}}$ , circle), neon ( $D_{\text{Ne}}$ , diamond) and argon ( $D_{\text{Ar}}$ , triangle). The measurements on ice single crystals and those on ice polycrystals are represented by open and solid symbols, respectively. Each bar shows the experimental error range. Some error bars were smaller than the symbol.

The values of  $D_{\text{He}}$  ranged between  $1.0 \times 10^{-9}$  and  $1.2 \times 10^{-9}$   $\text{m}^2 \text{s}^{-1}$ . In this temperature range, we did not find a remarkable temperature dependence of  $D_{\text{He}}$ . The value of  $D_{\text{He}}$  in ice single crystals coincided with that in ice polycrystals at  $T=263.2$  K. On the other

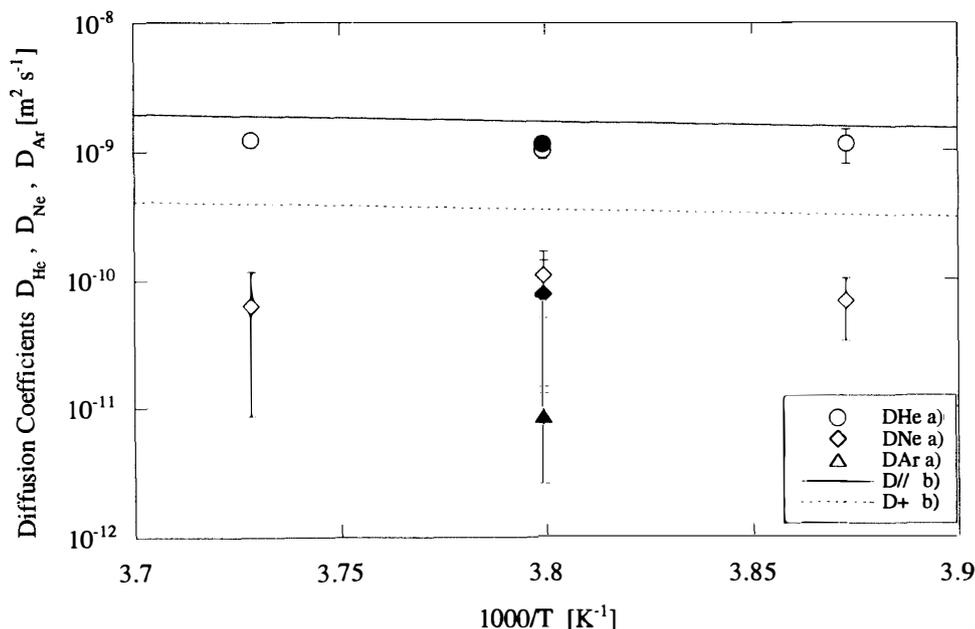


Fig. 3. Diffusion coefficient of helium ( $D_{\text{He}}$ ), neon ( $D_{\text{Ne}}$ ) and argon ( $D_{\text{Ar}}$ ) in ice depending on temperature  $T$ . a) the present study: Each explanatory note is  $D_{\text{He}}$ : circle,  $D_{\text{Ne}}$ : diamond and  $D_{\text{Ar}}$ : triangle. The diffusion coefficients in a single ice crystal are denoted by open symbols, and those in polycrystalline ice by solid symbols. Each error bar shows the experimental error range. b) HAAS et al. (1971): the solid line and dotted line are the diffusion coefficient of helium through ice single crystal parallel to  $c$ -axis,  $D_{//}$  and perpendicular to  $c$ -axis,  $D_{\perp}$ , respectively.

hand,  $D_{\text{Ne}}$  ranged between  $6.2 \times 10^{-11}$  and  $1.1 \times 10^{-10}$   $\text{m}^2 \text{s}^{-1}$ . The variations of  $D_{\text{Ne}}$  with temperature and with the ice sample were observed to be small. Therefore, we concluded that the temperature dependence of both  $D_{\text{He}}$  and  $D_{\text{Ne}}$  was small in this temperature range and that there was only a small difference between  $D_{\text{He}}$  and  $D_{\text{Ne}}$  in ice single crystals and in ice polycrystals. For argon gas measurements, we could obtain only one diffusion coefficient in ice polycrystals due to the very small diffusion rate,  $D_{\text{Ar}}$ , which is of order  $10^{-11}$   $\text{m}^2 \text{s}^{-1}$ .

The solubilities of helium,  $S_{\text{He}}$ , and neon,  $S_{\text{Ne}}$ , in ice samples are determined in molar fraction and are shown in Fig. 4 at various temperatures. The explanatory notes are the same as for Fig. 3. This figure shows that  $S_{\text{He}}$  ranged between  $1.8 \times 10^{-6}$  and  $3.3 \times 10^{-6}$ . Significant dependence of  $S_{\text{He}}$  on temperature was not found in this temperature range. The solubility of neon and argon gas could not be measured precisely because the pressure did not reach equilibrium during the experimental period (more than 10 days). We estimated  $S_{\text{Ne}}$  from the curve fitted to eq. (2) to range from  $2.7 \times 10^{-7}$  to  $4.5 \times 10^{-7}$ , almost 10 times smaller than  $S_{\text{He}}$ . However, we cannot estimate  $S_{\text{Ar}}$  because the estimation from eq. (2) includes large errors for argon gas.

The diffusion coefficients of three noble gases in ice were obtained in various conditions. We compared  $D_{\text{He}}$ ,  $D_{\text{Ne}}$  and  $D_{\text{Ar}}$  in polycrystalline ice at about 263.2 K. Figure 5 represents the dependence of diffusion coefficients on the van der Waals radius  $R$  of each gas molecule ( $D_{\text{He}}$ : solid circle,  $D_{\text{Ne}}$ : solid diamond, and  $D_{\text{Ar}}$  solid triangle). This figure indicates that the diffusion coefficient  $D$  decreases with increasing  $R$ . The relation

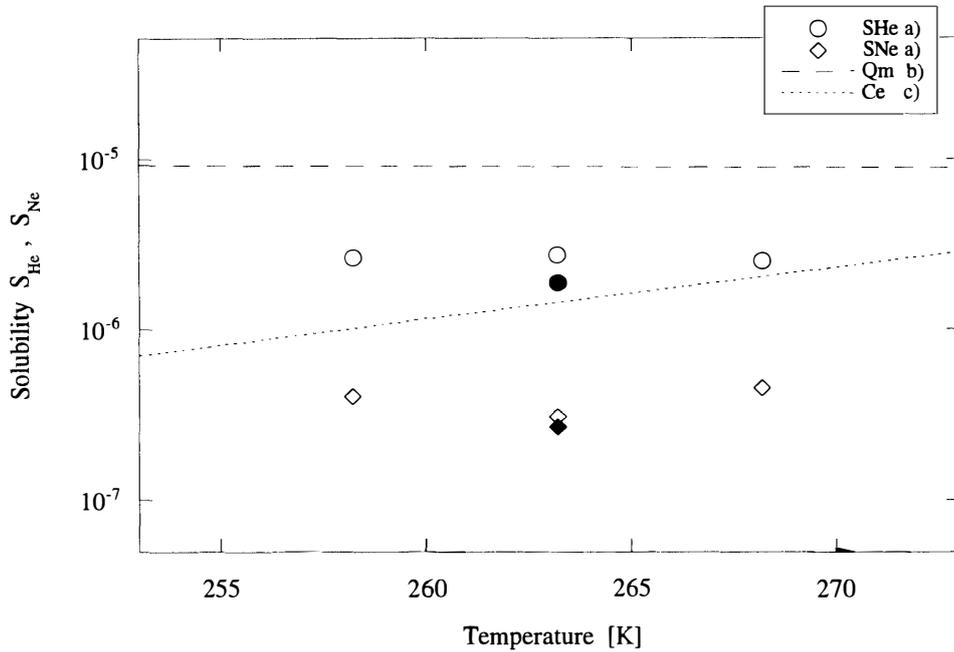


Fig. 4. Temperature dependence of solubility of helium ( $S_{He}$ ) and neon ( $S_{Ne}$ ). a) the present study, b) HAAS *et al.* (1971): the dashed line shows the linear extrapolation of the solubility of helium  $Q_m$ , and c) GOTO *et al.* (1986) the dotted line is the equilibrium concentration of interstitial water molecules  $C_e$  in ice single crystals.

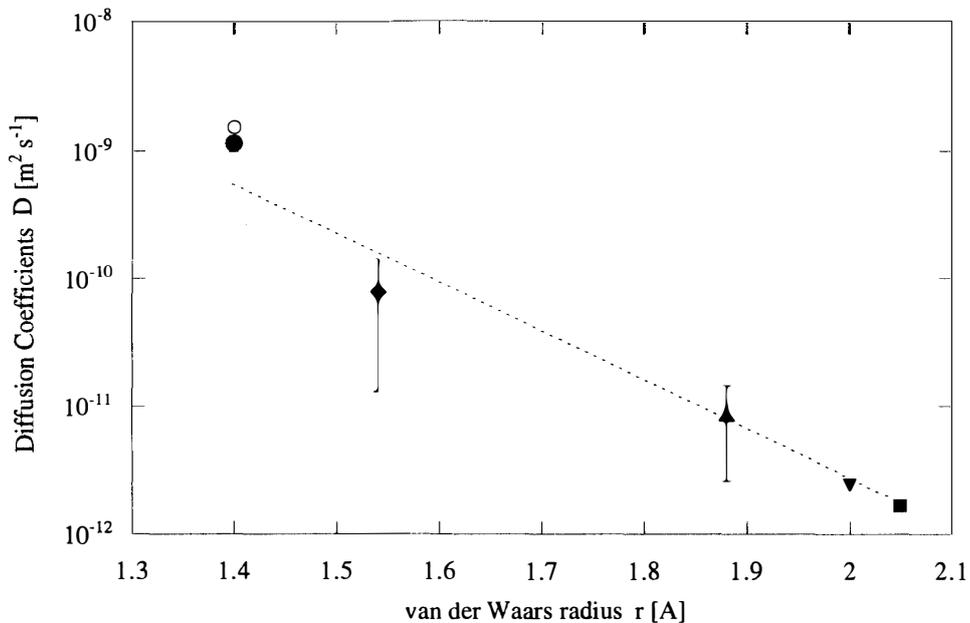


Fig. 5. Diffusion coefficients  $D$  in polycrystal ice vs. molecular radius  $R$  at 263.2 K.  $D_{He}$ ,  $D_{Ne}$  and  $D_{Ar}$  are shown by a solid circle, solid diamond, and solid triangle, respectively,  $D_{H_2O}$  is an open circle calculated from the equation of GOTO *et al.* (1986) and  $D_{N_2}$  and  $D_{O_2}$ , estimated by extrapolation of the dashed line, are a solid up-side-down triangle and solid square, respectively.

between  $D$  ( $\text{m}^2 \text{s}^{-1}$ ) and  $R$  (m) is obtained by the least square method as:

$$D = 4.0 \times 10^{-4} \exp(-9.5 \times 10^{10} R). \quad (3)$$

This equation indicates that the diffusion coefficients of gas molecules are affected by their van der Waals radii. Then we can estimate the diffusion coefficient of larger molecules such as nitrogen and oxygen by extending this equation.

## 4. Discussions

### 4.1. Diffusion coefficient of helium gas in ice

We obtained the diffusion coefficients of helium in ice single crystals and polycrystals. HAAS *et al.* (1971) measured the diffusion coefficient of helium gas diffusing out from a ice single crystal. They found that the diffusion coefficient depends both on temperature and on the ice crystal orientation. The temperature dependence of the diffusion coefficient  $D$  can be represented by the following equation:

$$D = D_0 \exp(-E / kT), \quad (4)$$

where  $D_0$  is a constant,  $E$  is the activation energy,  $k$  is the Boltzmann constant and  $T$  is the absolute temperature. The constants of diffusion coefficient of helium through the ice crystal are  $D_{0\parallel} = 3.4 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  and  $E_{\parallel} = 0.12 \text{ eV}$  for the direction parallel to the  $c$ -axis, and  $D_{0\perp} = 1.1 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$  and  $E_{\perp} = 0.13 \text{ eV}$  for the direction perpendicular to the  $c$ -axis. These values are shown in Fig. 3 by solid and dotted lines, respectively. In the present study,  $D_{\text{He}}$  should range between  $D_{\parallel}$  and  $D_{\perp}$  because ice samples were prepared so that the diffusion coefficient would not be affected by the crystal orientation. The obtained values of  $D_{\text{He}}$  ranged between these values. This shows that the present experimental method is adaptable quantitatively for measurements of diffusion coefficients of gas molecules in ice.

### 4.2. Molecular size dependence of diffusion coefficients

The mechanism of self-diffusion in ice crystals is an interstitial one (GOTO *et al.*, 1986). If the size of a gas molecule is as small as that of a water molecule, the gas molecule can diffuse through the ice crystal as the self-interstitial. The comparison of molecular sizes with the channel diameter in ice crystals was listed by HONDOH and UCHIDA (1992). They indicated that a helium molecule could diffuse smoothly through the ice crystal, but an argon molecule diffuses with difficulty. Then, the diffusion coefficient should decrease with increase in the molecular size. Figure 5 shows that diffusion coefficients of noble gases decrease exponentially with increase of their van der Waals radii as shown in eq. (3).

The self diffusion of water molecules in ice crystals,  $D_{\text{H}_2\text{O}}$ , has been measured by X-ray diffraction (GOTO *et al.*, 1986). The authors found that the temperature dependence of  $D_{\text{H}_2\text{O}}$  obeys eq. (4). For water molecules,  $D_{0\text{H}_2\text{O}} = 1.8 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$  and  $E_{\text{H}_2\text{O}} = 0.16 \text{ eV}$ . Using this equation, we obtained  $D_{\text{H}_2\text{O}}$  to be about  $1.6 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  at  $T = 263.2 \text{ K}$ . As shown in Fig. 5 by the open circle, this value coincides well with the empirical eq. (3)

obtained in the present study.

Using eq. (3) and the molecular size data, we can estimate the diffusion coefficients of nitrogen molecules,  $D_{N_2}$ , and of oxygen molecules,  $D_{O_2}$ , through the ice crystals. Since the molecular diameters of nitrogen and oxygen are  $2.05 \times 10^{-10}$  m and  $2.10 \times 10^{-10}$  m, respectively,  $D_{N_2}$  is calculated as approximately  $1.4 \times 10^{-12}$  m<sup>2</sup> s<sup>-1</sup> and  $D_{O_2} = 8.7 \times 10^{-13}$  m<sup>2</sup> s<sup>-1</sup>. This value is lower than the detection limit of the present measurements. Although a previous study (SATOH *et al.*, 1994) predicted that  $D_{N_2} \approx 10^{-10}$  m<sup>2</sup> s<sup>-1</sup>, this value is  $10^2$  times larger than that estimated from eq. (4). This disagreement may have occurred because the previous study overestimated the value of  $D_{N_2}$  due to the lower detection limit than that of the present study.

The estimated values of  $D_{N_2} \approx D_{O_2} \approx 10^{-12}$  m<sup>2</sup> s<sup>-1</sup> indicate that air molecules included in ice core samples can escape from the ice sample. The diffusion distance of air molecules is estimated from Newton's relation to be about 5 cm for 40 years. If there are some cracks in ice cores, air molecules can escape more easily. This indicates that if ice core samples are stored at temperature of about 263.2 K for a long time, the amount of air molecules including in the samples might change from the original value.

#### 4.3. Solubility of noble gas molecules in ice

The solubility of helium gas,  $Q_m$ , has been measured by HAAS *et al.* (1971) at temperatures lower than 232.2 K. The linear extrapolation of their results to high temperatures (dashed line in Fig. 4) shows that  $Q_m$  is about  $9 \times 10^{-6}$ , and that its temperature dependence is very small. The temperature dependence of  $S_{He}$  is similar to that of  $Q_m$ . However, the quantity of  $S_{He}$  is about 1/4 of  $Q_m$ . On the other hand, KAHANE *et al.* (1969) obtained the solubility of helium. They reported the solubility to be approximately 1.5 times as large as  $Q_m$  and 6.4 times as large as  $S_{He}$ . The disagreement of these values may have resulted from the experimental errors. The small value of  $S_{He}$  compared with  $Q_m$  is, however, considered to have resulted from  $S_{He}$  being measured at pressure  $P_2$ , whereas  $Q_m$  was measured at pressures below atmospheric. The difference of measurement pressure will change the equilibrium quantity of gas molecules in the ice sample.

There are only a few measurements of solubility of neon. KAHANE *et al.* (1969) reported the solubility of neon gas in ice, which was  $1.4 \times 10^{-5}$  at 248.2 K. This value is approximately  $10^2$  times as large as  $S_{Ne}$ . The disagreement of these values may have resulted from the overestimation of the previous study, as happened for helium measurements, or our underestimation of  $S_{Ne}$  from the  $P$ - $t$  curve due to the small diffusion rate of neon gas in ice.

We compare the solubility of noble gases with the concentration of the self-interstitial of ice. The equilibrium concentration of the self-interstitial,  $C_e$ , has been determined by the X-ray topography method (GOTO *et al.*, 1982). The authors found that  $C_e$  depends on temperature:

$$C_e = q \exp(S_f/k) \exp(-E_f/kT), \quad (5)$$

where  $q$  is the number ratio of interstices to the regular sites of water molecules in the ice lattice, which is 0.5 for ice. The formation energy  $E_f$  was determined to be 0.40 eV and the formation entropy  $S_f = 4.9 k$  ( $4.2 \times 10^{-4}$  eV K<sup>-1</sup>). In Fig. 4,  $C_e$  is represented by the

dotted line. At about 263.2 K,  $C_e$  is about  $1.5 \times 10^{-6}$ . This value coincides well with  $S_{\text{He}}$ , and is about 10 times as large as  $S_{\text{Ne}}$ . As the van der Waals diameter of helium molecules is similar to that of water molecules, the solubilities of both types of molecules may be similar.

The diffusion rate of air molecules in a deep ice sheet has been estimated from the growth rate of air-hydrate crystals (UCHIDA *et al.*, 1994). They found the value of the product of the diffusion coefficient and the solubility of air molecules to be on the order of  $10^{-19} \text{ m}^2 \text{ s}^{-1}$  at depths below 1000 m. Since the present study cannot reveal the solubility of argon gas, we assume that the solubility of gas molecules larger than the ice channel may be similar to  $S_{\text{Ne}}$ . If the solubilities of nitrogen and oxygen in ice are as small as that of neon, the products of the diffusion coefficient and the solubilities of both types of molecules in ice are  $D_{\text{N}_2} S_{\text{N}_2} \approx 4 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$  and  $D_{\text{O}_2} S_{\text{O}_2} \approx 3 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ , respectively. These values coincide well with the value of  $D_{\text{air}} S_{\text{air}}$ .

### Acknowledgments

The authors wish to thank Dr. J. OCAMPO, Dr. N. AZUMA, Dr. K. GOTO-AZUMA and Dr. A. HIGASHI for their helpful discussions.

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(Received December 21, 1995; Revised manuscript accepted February 29, 1996)