each crystal which started from the individual nucleus interacts with each other and is hindered from growing in all three [1120] directions. As a result, each crystal is expected to grow preferentially to one of the [1120] directions at the interface, as shown by the dotted lines in Figure 14. But as another layer is added, a possibility will exist for an oxygen atom to be placed upon the position of a solid triangle instead of being placed on an open circle. This stacking sequence is, in other words, a stacking fault parallel to the basal plane. If such a fault is introduced in sequence several times, the resultant stacking order of the polycrystalline snow crystal; and a possibility of the formation of a cubic embryo has been theoretically discussed by Takahashi.14

Our results obtained by the X-ray Laue method concerning crystallographic orientation of individual crystals support such a stacking sequence. Moreover the existence of two kinds of crystals each orienting themselves in the opposite directions in a uniform interference color provides information about the surface roughness, namely, the surface topography of the ice surface. Suppose that crystallization takes place simultaneously at the interface. Then, for the growth of the two different crystals mentioned above, there must exist a step at the interface whose height is at least $c/2$, where $c$ is the unit length along the c axis of the ice Ih.

The roughness of the surface resulting from the foregoing and other causes is made smooth possibly by being covered with the quasi-liquid layer at temperatures above $-10 \, ^\circ C$; however, with falling temperature the surface becomes bare of such a layer and acts as a nucleation site.

**Concluding Remarks**

Crystallographic relationships were determined directly between a frozen droplet and the ice substrate on which it was frozen by using X-ray Laue photography and polarizing light microscopy. Consequently, new light was shed on how much an effect the temperatures and orientation of the ice substrate have on polycrystallization of the water droplet.

As for the prismatic plane of the substrate, the droplet always froze on it as a single crystal with the same orientation as that of the substrate when the environmental temperature was not below $-20 \, ^\circ C$. At lower temperatures polycrystallization occurred sometimes, but no regularity was observed in the structure and orientation of the crystal.

Meanwhile, as for the basal plane, not only the structure but also the number of crystals in the frozen droplet depended strongly on the temperature. In the case of polycrystallization on the basal plane, a droplet froze in the following manner: one of the a axes of any given crystal in a frozen droplet coincided with one of the a axes of the substrate, whereas the c axis of the former was tilted exactly by 70.5° from that of the latter regardless of the form and the number of crystals. An interpretation of this crystal structure and orientation was given by considering dendritic growth which would occur in highly supercooled water.

It was observed that the number of crystals in a frozen droplet increased with falling temperature above $-18 \, ^\circ C$ and that below that temperature individual crystals in the specific crystallographic relations with respect to the basal plane of the substrate arranged themselves so as to give a new hexagonal symmetrical Laue pattern. It is supposed from this observation that the temperature has an influence on the characterization of surface structure, namely, topography.

Monocrystallization at temperatures above $-10 \, ^\circ C$ is caused not only by the relatively small degree of supercooling but also by the real structure which is expected to be covered with the quasi-liquid layer. With falling temperature, the coverage and the thickness of the quasi-liquid layer decrease rapidly, which gives rise to a rapid increase in the number of crystals at temperatures between $-12$ and $-18 \, ^\circ C$. The experimental results suggest that at $-18 \, ^\circ C$ the surface of the basal plane becomes bare of the quasi-liquid layer and that at lower temperatures the structure of this bare surface does not undergo a further significant change.

**Registry No.** Water, 7732-18-5.

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**Modification of the Surface Structure of Ice during Ageing**

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Adsorption isotherms of $N_2$ and $CO_2$ on ice have been measured on different ice surface preparations. For hexagonal ice the adsorption capacity diminishes with time. This effect is more important for cleaved surfaces and high annealing temperatures. The influence of a "quasi-liquid" surface layer and grain size is discussed.

**Introduction**

Faraday¹ was the first to propose that the surface of ice is covered by a liquidlike layer. The structural and dynamic studies done since this work have been reviewed by Jellinek.² Fletcher³ established a semiquantitative thermodynamic model for an anomalous quasi-liquid transition layer on the surface of ice near the melting point. This surface layer is supposed to thicken rapidly with increasing

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Differences of one order of magnitude are currently found in the literature. The purpose of the present study is to examine the surface structural rearrangements of hexagonal ice by means of adsorption more carefully than previously (Ocampo and Klinger). The idea was that the intrinsic surface rearrangement is time and temperature dependent. Special attention is given to the properties of freshly cleaved surfaces. This last point is particularly important for geochemical investigations. In fact several authors attempted to measure the CO$_2$ content of quaternary paleoatmospheres by analyzing gas inclusions of polar ice sheets up to 300,000 years old (Delmas et al., Berner et al.). For extracting the gas of the bubbles, those authors crushed the ice in a vacuum chamber and analyzed the gas composition by means of gas chromatography. If there is selective adsorption for some components of the gas mixture the final result may be affected by a systematical error.

Adsorption studies in general have provided a useful approach for the characterization of surfaces. We must be cautious, however, when we try to give an interpretation of thermodynamic quantities such as heats and entropies of adsorption. This is particularly true if we have the usual situation of heterogeneous surfaces or if the state of the adsorbent is affected by the adsorbate (Adamson).

**Experimental Section**

The classical manometric method was used for the measurement of CO$_2$ and N$_2$ adsorption isotherms. As the amount of adsorbed gas is rather small we specially designed an apparatus for our measurements. A detailed description of this apparatus is given in a previous paper.6

In order to avoid systematic errors on the CO$_2$ isotherms due to thermal gradients in the system we maintained the same temperature in the whole apparatus, pressure gauges included. A further problem was the measurement of the dead space volume. Helium is not usable for dead space calibration as it diffuses through the ice matrix. For temperatures higher than 220 K we sometimes use krypton as calibration gas (at low temperatures krypton is adsorbed on ice). In a general manner we measured "relative" CO$_2$ isotherms. To do this we used the smallest dead space volume that gave positive adsorption isotherms.

The specific surface areas of the samples were deduced from nitrogen adsorption isotherms at liquid nitrogen temperature.11 Two different methods were used for sample preparation. The first type of sample was obtained by condensing water vapor in a Pyrex glass vessel at liquid nitrogen temperature. The ice obtained in this way was probably amorphous. The sample was then annealed at 200 K in order to obtain hexagonal ice. The samples were then submitted to different annealing cycles. The second type of hexagonal ice samples was obtained by crushing of compact hexagonal ice samples under vacuum in a ball mill container at 257 K. Immediately after crushing, we cooled the samples to liquid nitrogen temperature in order to avoid alteration of the freshly cleaved ice surfaces. The ice used was natural polycrystalline ice from D57, Antarctica (68°S, 137°E).

**Results**

Nitrogen adsorption isotherms at 77 K on vapor deposition and cleaved ice (see Table I).

All the samples were annealed by bringing them to a temperature higher than 77 K for a desired time. Before the measurement they were recooled to 77 K for the adsorption measurements.

In Table I we have summarized the following parameters: specific surface area $S_w$, radii of the grains $r$ (if they are supposed to be spherical), BET constant $C$ and the net heat of adsorption $\Delta Q$, time of ageing $\Delta t$, and annealing temperature $T$. The kind of sample preparation and phase transformations is also given in the same table. An inspection of that table shows four types of hexagonal samples: natural snow samples (6A), natural cleaved samples

### Table I: Nitrogen Adsorption at 77 K on Annealed and Aged Ice (See Figure 1)

<table>
<thead>
<tr>
<th>run</th>
<th>phase</th>
<th>$T$, K</th>
<th>$\Delta t$</th>
<th>$S_w$, m$^2$/g</th>
<th>$r$, $\mu$m</th>
<th>$C$</th>
<th>$\Delta Q$, cal/mol</th>
<th>preparatn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1A</td>
<td>cubic</td>
<td>186</td>
<td>12 h</td>
<td>14</td>
<td>0.2</td>
<td>46.8</td>
<td>595</td>
<td>from amorphous</td>
</tr>
<tr>
<td>1B</td>
<td>hexagonal</td>
<td>243</td>
<td>10 min</td>
<td>0.12</td>
<td>25.0</td>
<td>11.2</td>
<td>37.5</td>
<td>from 1A</td>
</tr>
<tr>
<td>1C</td>
<td>hexagonal</td>
<td>271</td>
<td>10 min</td>
<td>0.12</td>
<td>25.0</td>
<td>8.8</td>
<td>22.5</td>
<td>from 1B</td>
</tr>
<tr>
<td>2A</td>
<td>hexagonal</td>
<td>248</td>
<td>90 min</td>
<td>0.49</td>
<td>6.1</td>
<td>68.0</td>
<td>645</td>
<td>from cleaved natural ice D57 138</td>
</tr>
<tr>
<td>3A</td>
<td>hexagonal</td>
<td>247</td>
<td>3 min</td>
<td>0.68</td>
<td>4.4</td>
<td>320.5</td>
<td>883</td>
<td>from cleaved natural ice D57 145</td>
</tr>
<tr>
<td>3B</td>
<td>hexagonal</td>
<td>257</td>
<td>4 days</td>
<td>0.27</td>
<td>11.0</td>
<td>5.3</td>
<td>255</td>
<td>from 3A</td>
</tr>
<tr>
<td>4A</td>
<td>cubic</td>
<td>153</td>
<td>30 min</td>
<td>1.6</td>
<td>1.9</td>
<td>95</td>
<td>700</td>
<td>from amorphous</td>
</tr>
<tr>
<td>4B</td>
<td>hexagonal</td>
<td>223</td>
<td>1 h</td>
<td>0.22</td>
<td>13.6</td>
<td>8</td>
<td>320</td>
<td>from 4A</td>
</tr>
<tr>
<td>5A</td>
<td>hexagonal</td>
<td>193</td>
<td>30 min</td>
<td>0.4</td>
<td>7.5</td>
<td>20</td>
<td>460</td>
<td>from amorphous</td>
</tr>
<tr>
<td>6A</td>
<td>hexagonal</td>
<td>fully annealed</td>
<td>0.2</td>
<td>15.0</td>
<td>0.8</td>
<td>natural snow</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ For comparison from Adamson et al.9

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Figure 1. Nitrogen adsorption isotherms at 77 K on vapor depositions and cleaved ice (see Table I).
Modification of the Surface Structure of Ice

Clathrates by solid–gas interaction on the surface of macroscopic single crystals (volumes from 1 to 180 cm$^3$). The surface/volume ratios varied from 2 to 7 and the waiting time from 1 to 23 days. The interesting temperature range was then corresponding to the high mobility of water ice surface molecules: i.e., greater than 238 K. After doping, we heated the sample to a temperature higher than the decomposition temperature and measured the volume of the returned gas\(^{14}\).

The rate $K_i$ of clathrate formation measured on single crystals for a surface area $S_i$ is (Ocampo\(^{14}\))

$$K_i = \frac{\gamma_i T}{273\Delta x (P - P_w)} \quad (1)$$

where $\gamma_i$ is the outgassing volume of CO$_2$ per ice surface unity after a time $\Delta t$, $P_w$ is the clathrate equilibrium pressure at the temperature $T$, and $P$ is the pressure at the initial time.

At 258 K, we have a rate of $4 \times 10^{-9}$ and $2 \times 10^{-7}$ cm/s at 269 K.

**Discussion**

We believe that our results may be explained in the following way: Initially at 77 K the ice surfaces are composed of undistorted cleavage planes where we may expect a statistical mixture of surface oxygen atoms and hydroxyl groups. The intrinsic surface rearrangement must occur during ageing. As the annealing temperature increases, the higher mobility of water molecules at the surface of ice further reduces the polar nature of the surface. The evolution of the isotherms from Type II to Type III seems to be due to a rearrangement of surface dipoles in an irreversible manner.

For temperatures lower than 238 K the CO$_2$ adsorption isotherms on hexagonal ice (Ocampo et al.\(^{6}\) Adamson et al.\(^{15}\)) are approximately linear. The adsorption is low until a clathrate region is attained. The net adsorption heat is positive and the BET C constant is greater than two. Furthermore, the adsorption heat is near the condensation heat of CO$_2$. This shows a classical physical adsorption.

If we measure the specific surface area with CO$_2$, we find a value smaller than that measured with nitrogen at 77 K.

\(\text{(2A, 3A, and 3B), different preparation obtained by vapor deposition (4B and 5A), and vapor deposition samples that have been remeasured after several annealing cycles (1B and 1C). From Figure 1, we observe that the adsorption capacity diminishes irreversibly during ageing. The initially type II isotherms change to type III and the net adsorption heats fall more abruptly for high annealing temperatures than for low ones (runs 1B and 1C). We call this behavior the intrinsic restructuring of the surface in the sense that the surface is not affected by the adsorption of nitrogen at 77 K. It seems from runs 1A and 4A that for the smallest grain size we have the lowest net adsorption heat after ageing. This is generally accompanied by a reduction of the specific surface area.}

\(\text{CO}_2\text{ adsorption isotherms on hexagonal ice at temperatures higher than 220 K were performed and the isosteric heats of adsorption } q_s \text{ and differential molar entropies } \Delta S \text{ measured for different surfaces coverages}

\[\Delta S = -\frac{(q_s - Q_L)}{T} - R \ln X\]

\(\text{The sample for the } \text{CO}_2\text{ adsorption measurements was also prepared from amorphous deposition at the liquid nitrogen temperature. The annealing temperature has been 233 K for 5 min. The specific surface of 2.8 m}^2\text{/g in the amorphous state diminishes to 0.6 m}^2\text{/g in the hexagonal phase. In the same way the net adsorption heat falls from 560 to 302 cal/mol.}

\(\text{The anomalous } \text{CO}_2\text{ adsorption isotherms (growing with increasing temperatures) were discussed earlier.}^6 \text{ Other unusual adsorption isotherms, } n\text{-hexane and } n\text{-pentane on hexagonal ice (Orem et al.}\text{)}^{12}\text{ and ammonia on graphitized carbon blacks (Bomchil et al.}\text{)}^{13}\text{, show the same behavior.}

\(\text{Figure 2 shows the isosteric heats of adsorption and entropies for the corresponding adsorption isotheres of Figure 3.}

\(\text{In order to understand the kinetics of extrinsic restructuring of the ice surfaces with CO}_2\text{ we have formed}

\(\text{(12) M. Orem and A. W. Adamson, J. Colloid Interface Sci., 31, 278 (1969).}


\(\text{(14) J. Ocampo, Thèse de 3e cycle, USMG, Grenoble, France, 1980.}

\(\text{(15) A. N. Adamson and B. R. Jones, J. Colloid Interface Sci., 37, 881 (1971).}

\(\text{(16) W. Drost-Hansen, J. Colloid Interface Sci., 25, 131 (1967).}\)
Moreover, this apparent surface area "increases" with temperature. This means that the number of physical adsorption sites for CO₂ increases. At approximately 233 K the surface measured with CO₂ is the same than that measured with nitrogen at 77 K. The number of sites seems to be saturated at this temperature. On the other hand, the surface of the ice must be subject to a restructuring due to the adsorbate (extrinsic restructuring) as we show below.

For temperatures higher than 233 K the type III CO₂ isotherms transform to linear isotherms again. The BET C constant and the net heat of adsorption measured with CO₂ are C \simeq 1 and \Delta Q < 0. Moreover, the apparent specific surface area measured with CO₂ at temperatures higher than 233 K is greater than that measured with nitrogen at 77 K, and grows with increasing temperatures. It means that clathration may be occurring.

In our case the isosteric heats of adsorption qₚₑ are generally lower than the liquefaction heat. They diminish also with coverage. From BET theory we expect the formation of molecular groups of several layers in isolated region if \Delta Q < 0. Moreover, qₚₑ diminishes with coverage. This means that the adsorption of CO₂ starts in the most active sites. The differential entropies are greater than those of the liquid state and grow with coverage. The entropy also approaches that of the liquid state with rising temperature. In other words, the mobility of CO₂ molecules in the localized adsorption sites is greater than that of liquid CO₂. We think that the first molecules striking the active sites diffuse into depth where they are more rigid than on the surface. The number of these active sites seems to depend on the crystal history. On the other hand, the depth of the sites is temperature dependent and limited by a liquid-like layer.

Orem et al.¹² found the same behavior on the n-hexane-ice system with the difference that the net heat of adsorption is greater than that of gas-liquid condensation. The n-hexane molecule is too big to form a clathrate, so it does not diffuse to the depth as CO₂ does.

Conclusion

As was pointed out before, the intrinsic nature of the hexagonal ice surfaces is that in which undistorted cleavage planes cannot exist in equilibrium at temperatures near the melting point.

The surface of the vapor deposition preparations in amorphous and cubic states show a local dipolar field lower than the local dipolar field of fresh hexagonal cleaved surface. Moreover, the cleaved surfaces diminish its adsorption capacity with time. This effect is more important for high annealing temperatures than for low ones (influence of the "quasi-liquid" surface layer). The kinetics of this surface ageing seems to be inversely dependent on the grain size. A systematic ageing at a constant temperature is needed to study the kinetics of this phenomenon. This surface restructuring with time may be activated by the large-amplitude thermal vibration of the oxygen atoms⁴ and propagates itself by cooperative fluctuations from metastable sites at the surface to the interior of the bulk ice. The speculations about the extrinsic restructuring of the ice surface, made from CO₂ isotherms, agree with the fact that the metastable sites may be of a dislocation type where polar structures are involved.¹⁶ The number and depth of these sites increases with temperature and seem to be very active for the CO₂ molecule.

The homogeneous disorder may be frozen at low temperatures and in this way the ice surface becomes less adsorbent to nitrogen at nitrogen temperatures.

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Registry No. CO₂, 124-38-9; N₂, 7727-37-9; water, 7732-18-5.

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**Optimal Conditions for the Homogeneous Nucleation of Cubic Ice from Concentrated Solutions of LiCl-D₂O**

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Controlled conditions for the nucleation of ice from concentrated electrolyte solutions can be achieved by choosing concentrations such that the homogeneous nucleation temperature T_H lies very close to the glass transition temperature T_g. We may obtain T_H from experiments using emulsions of the electrolyte solutions, but T_g is almost constant at 142 K for concentrations above 9 mol % LiCl. Heat treatment a few degrees below T_g permits nucleation of ice, whereas above T_g growth of the nuclei can be observed and followed by small angle neutron scattering. We have also measured the evolution of the diffraction spectra using a high-flux neutron diffractometer, and identified the conditions for growth of the metastable cubic phase of ice, and its transformation to the stable hexagonal phase, Ih. Cubic ice, Ic, is favored at concentrations between 9 and 12 mol % LiCl where it precipitates near T_g. Cubic ice is always found as very small crystallites, <300 Å in diameter. It transforms to hexagonal ice at higher temperatures as the crystallite size increases due to ripening.

Significant progress has recently been made in our understanding of ice crystallization from glassy aqueous electrolytes¹². The key point is the concentration dependence of the temperature for homogeneous nucleation...