Permeation of Gases through Ice

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(Manuscript received September 9, 1958)

Abstract

The permeation rate of carbon dioxide and oxygen through ice has been determined at several temperatures. At $-9.5°$ C the carbon dioxide permeation constant was found to be 0.7×10^{-11} cm^2 sec^{-1} atm^{-1}, which is about two million times less than in water. The permeation increased hyperbolically towards 0° C. No permeation of oxygen through the ice could be detected. It is concluded that the gas penetrates the ice through intercrystalline brine films rather than through the ice crystals.

Knowledge of the permeability of gases through ice is useful on several scores. It has been shown that many northern plants and animals survive the winter frozen solid, some of them with 90 % or more of the water frozen to ice, and yet slow but measurable respiration continues down to $-20°$ or lower. A great many aquatic animals and plants have also been found to survive within the ice of bottom frozen arctic lakes and ponds. Since, demonstrably, freezing of the organism does not stop the respiration, the question arises whether gas exchange can possibly take place through the ice which entombs the organism. A few determinations undertaken by SCHOLANDER, FLAGG, HOCK and IRVING (1953) showed that in general this cannot be so, for the ice is extremely gas tight, indeed as tight as is glass to helium (NORTON, 1957).

This opened up the interesting possibility that gas bubbles enclosed in ice might under ideal conditions remain unchanged for very long times, perhaps millenia. The whitish colour characteristic of icebergs is caused by masses of gas bubbles dispersed throughout the ice. If these were formed by trapping of air when the snow was compacted to form the glacier, analysis of the bubbles might accordingly give information of the composition of ancient atmosphere. Such a possibility became even more challenging when it was demonstrated that glaciers can be radio-carbon dated through the content of carbon dioxide trapped in their bubbles (COACHMAN, HEMMINGSEN, SCHOLANDER, ENNS and DE VRIES, 1958). The validity of such determinations clearly depends upon how stable are the gases in the ice. One factor which could interfere is gas diffusion through the ice.

In the present investigation gas penetration through ice has been studied for carbon dioxide and oxygen at various temperatures. The method used is a modification on macro-scale of the micro method employed by SCHOLANDER et al. (1953). The macro scale has made possible greater accuracy in measurements of ice thickness and area and a more accurate gas analysis.

Methods

Principle. A thin ice sheet floats on mercury and separates carbon dioxide gas, or oxygen, above the ice sheet from a known volume of air deposited as a blister underneath the ice sheet. After a known period of time at constant

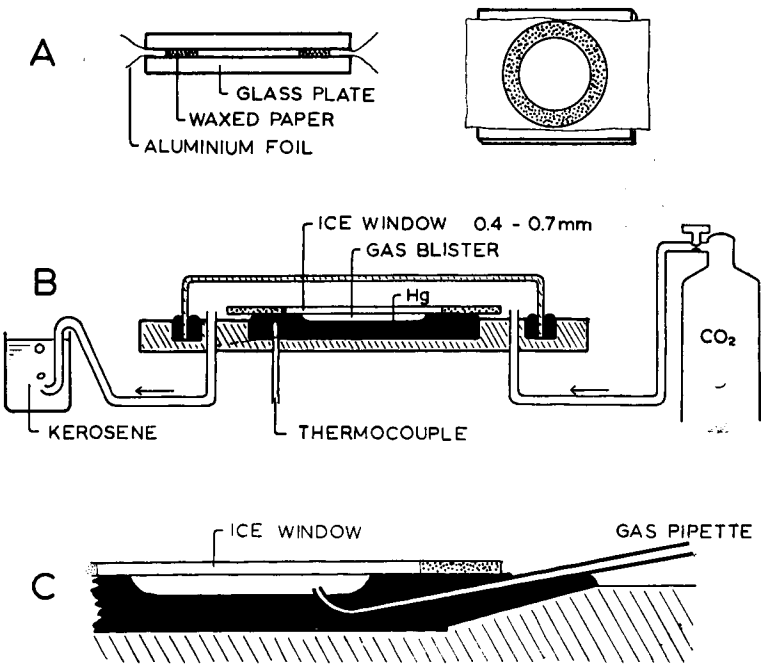

Fig. 1. Method for determination of the permeability of carbon dioxide and oxygen through ice.
A. Preparation of ice sheets.
B. Assembly for permeability measurements.
C. Introduction of gas under the ice sheet.

temperature the air is analyzed, and the amount of permeated gas is calculated in relation to ice thickness and blister area.

Experimental procedure. An ice membrane of uniform thickness was prepared between glass plates, spaced by a ring of waxed paper (Fig. 1, A). To prevent the ice from sticking, the glass plates were lightly greased and aluminum foil was smoothly rolled onto them. Boiled distilled water was flowed, while still hot, into the spacer ring between the plates, and left to freeze. When ready, the assembly was taken apart, and the foil was carefully stripped from the ice sheet. Only clear ice sheets containing an insignificant amount of air bubbles were used. The thickness of the ice was measured with a dial micrometer.

The ice window was floated on a pool of mercury, and a known volume of carbon dioxide-free air was delivered with a pipette under the ice, where it formed a shallow gas blister (Fig. 1, C). An inverted Petri dish, resting with its rim in mercury, formed an air-tight chamber over the ice, through which a continuous flow of carbon dioxide or oxygen could be maintained (Fig. 1, B). To minimize thinning of the ice by evaporation cracked ice was placed around the ice window. With this precaution the average thinning was reduced to 5—10 % of the total thickness. If the thinning was allowed to proceed much further, there was risk of local break through, especially at the warmer temperatures. The assembly rested in a thermostated box.

After a known period of time the gas blister was withdrawn and analyzed for carbon dioxide or oxygen, in a ½ cc gas analyzer, with an accuracy of ± 0.015 % (SCHOLANDER, 1947). The increase in carbon dioxide concentration was usually no more than about 0.03 %, i.e. barely above the accuracy of the gas analysis. Higher concentrations would have been desirable, but would require longer exposure with consequent danger of break through. The blister area remained clearly visible on the ice sheet, and was traced on transparent graph paper for measurement. The ice thickness was measured anew and averaged with the first measurement.

Determinations of the permeation were made at − 0.5°, − 1.5°, − 5.0° and − 9.5° C. At each temperature three to four experiments were performed, with a new ice membrane each time.

For oxygen determinations the same procedure was followed, using outdoor air in the blister and flowing pure oxygen through the chamber.

Calculations. The quantity of gas which penetrated the ice was calculated from the change in composition of the gas blister, disregarding the change in volume, which was too slight to be measured. According to Fick's law, the permeation constant K is given by the following equation:

$$K = \frac{q}{A \cdot t (P_1 - P_2)} d$$

where q is volume of permeating gas in cm^3, A is area of gas-ice contact in cm^2, t is time in seconds, d is thickness in cm, and $(P_1 - P_2)$ is the tension difference in atmospheres. The unit is accordingly $cm^3\ cm^1\ cm^{-2}\ sec^{-1}\ atm^{-1}$ and the dimensions $cm^2\ sec^{-1}\ atm^{-1}$.

Results and Discussion

The data pertaining to the carbon dioxide permeation at various temperatures are given in Table I and Figure 2. It will be seen that the carbon dioxide permeation increases very slightly from − 9.5° to − 1.5°, but rises steeply above − 1.5°.

Four determinations at − 5.0° and two at − 0.5° gave no measurable penetration of oxygen through ice. The permeation constant for oxygen was therefore less than 0.6×10^{-11} $cm^2\ sec^{-1}\ atm^{-1}$, which is the limit of accuracy of the method.

The permeation constant for carbon dioxide through water at 10° C is given as 1.7×10^{-5} $cm^2\ sec^{-1}\ atm^{-1}$ (HANDB. CHEM. PHYS.; BRUINS, 1929), i.e. carbon dioxide moves about one million times slower through ice at − 5° than through water.

The value for the permeation constant of carbon dioxide through ice at − 20° C was determined by SCHOLANDER et al. (1953) as 0.006 to 0.01 $mm^3\ mm^1\ cm^{-2}\ hour^{-1}\ atm^{-1}$, or transposed to the present units 1.7 to 2.8×10^{-10}, which is some ten times higher than was found in the present determinations at − 9.5°. This discrepancy is far beyond methodical uncertainties, and is most likely caused by impurities in the lake water used for the determinations (SCHOLANDER, personal communication). In agreement with the present determinations these authors found no penetration of oxygen through the ice.

Table 1. Permeation constant of carbon dioxide at various temperatures.

Temperature (° C)	Time (hours)	Ice-thickness (cm)	Bubble area (cm^2)	Bubble vol. (cm^3)	Permeated CO_2 (increase in vol. %)	Permeation constant × 10^{-11} ($cm^3\ cm^1\ cm^{-2}\ sec^{-1}\ atm^{-1}$)
— 0.5	10.0	0.072 ± 0.002	15.4 ± 0.1	2.10 ± 0.05	0.05 ± 0.01	14.4 ± 2.7
»	10.0	0.070 »	14.8 »	2.00 »	0.03 »	7.9 »
»	10.0	0.073 »	14.3 »	2.00 »	0.03 »	8.5 »
— 1.5	26.0	0.039 »	15.2 »	2.00 »	0.01 »	0.6 0.6
»	41.3	0.038 »	15.1 »	2.00 »	0.07 »	2.4 0.3
»	27.0	0.046 »	14.9 »	2.00 »	0.03 »	1.9 0.6
— 5.0	38.8	0.081 »	13.6 »	1.80 »	0.01 »	0.8 0.8
»	26.8	0.075 »	7.8 »	1.00 »	0.03 »	3.0 »
»	53.0	0.081 »	9.5 »	1.50 »	0.02 »	1.3 »
— 9.5	25.3	0.072 »	14.9 »	2.00 »	0.01 »	1.1 1.1
»	35.5	0.045 »	14.5 »	2.00 »	0.02 »	1.0 0.6
»	63.7	0.042 »	14.3 »	2.00 »	0.01 »	0.3 0.3
»	72.8	0.042 »	14.5 »	2.00 »	0.02 »	0.4 »
— 20	—	—	—	—	—	20* —
»	—	—	—	—	—	27* —
»	—	—	—	—	—	17* —

*) SCHOLANDER, FLAGG, HOCK and IRVING, 1953.

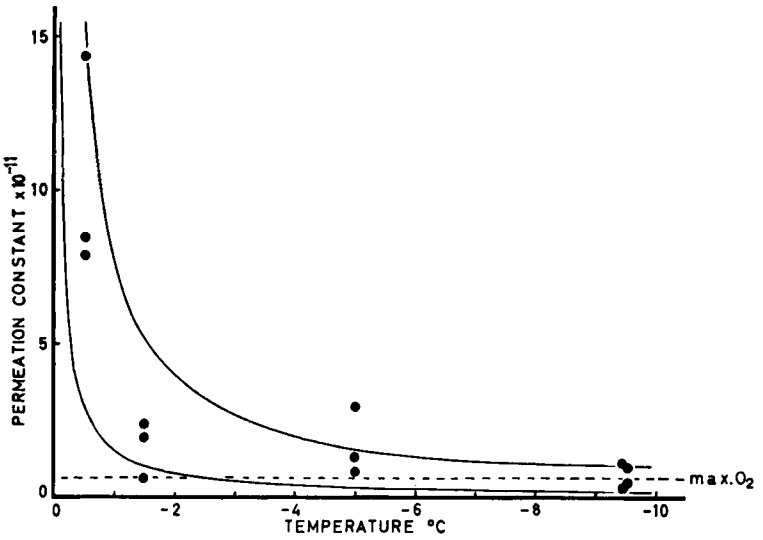

Fig. 2. Permeation of carbon dioxide through ice in relation to temperature. Dimensions of the permeation constant are $cm^2\ sec^{-1}\ atm^{-1}$. The data are compared to two arbitrary drawn hyperbolas. The oxygen permeation is less than the value indicated by the stippled line.

One may think of two possible pathways for the permeation of gas through ice, either through pores in a dry crystalline ice structure, or through a liquid phase which might exist in the ice. In the first case, according to Graham's law, one would expect that the smaller oxygen molecules would move through the ice in greater amount than the carbon dioxide molecules, but if permeation takes place through liquid pathways carbon dioxide would pass through in greater amount because of its 20—30 times greater solubility. The latter was clearly the case, and this strongly suggests that we are dealing with permeation through a liquid phase.

It has been established that impurities in the water, such as dissolved salts, concentrate as brine films on the surface of the ice crystals, when the water freezes (QUINCKE, 1905; DORSEY, 1940; RENAUD, 1949). The concentration of these films will very likely be proportional to the ice temperature below zero degrees Centigrade, and the volume of unfrozen brine will hence decrease hyperbolically with decreasing temperature. Since the brine channels are limited in length by the ice thickness, it follows that their cross section area must also decrease hyperbolically with temperature, and consequently also the gas permeation. Increase of brine concentration would slow down the permeation and would tend to accentuate the effect. It will be seen from Figure 2 that the data indeed approximate a hyperbolic temperature dependence of the permeation constant, and this, plus the fact that it is carbon dioxide rather than oxygen that penetrates the ice, furnishes independent support to the concept that permeation takes place through intercrystalline brine films.

Although the ice has a certain permeability for gases, it is justifiable to say that ice constitutes a rather tight barrier for the gas penetration. In a case like the radio-carbon dating of ice, this tightness to gases is of importance, since there must be no exchange of carbon dioxide between the atmosphere and the enclosed bubbles. Estimations based on the presented data show that this holds true, as exemplified by the following situation: A flat, cylindrical, horizontal gas bubble, 0.5 cm^3 in volume and with a top area of 1 cm^2 is situated in the ice 1 meter below the surface. The bubble has a pressure of 1 atm. and contains a gas mixture with 0.03 per cent or $1.5 \cdot 10^{-4}$ cm^3 carbon dioxide. Assuming solely a perpendicular permeation through the ice, and using Fick's law with a permeation constant of 10^{-11} $cm^2\ sec^{-1}\ atm^{-1}$, one will find that 10^{-6}

cm³ of carbon dioxide permeates from the atmosphere into the bubble in 1,000 years. This means that the enclosed carbon dioxide would be contaminated by about one percent of atmospheric carbon dioxide. With a permeation distance of 10 meters and a bubble pressure of 10 atm. the contamination would be about one hundredth of a per cent. With regard to the dating problem, an exchange of this order of magnitude is so small that it would be a negligible source of error.

Acknowledgement

The present investigation was supported by a grant from Arctic Institute of North America. I am greatly indebted to Professor P. F. Scholander for inspiring help during all stages of the work, and to Mr. L. K. Coachman for his stimulating interest.

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