

## SO<sub>2</sub> Uptake on Ice Spheres: Liquid Nature of the Ice-Air Interface

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The amount of SO<sub>2</sub> gas absorbed by ice of known surface area at equilibrium was used to estimate the volume of liquid water present at the ice-air interface at temperatures from -1 to -60°C. Calculations were based on Henry's law and acid dissociation equilibrium. The liquid volume is lowest at lower temperatures and ionic strength and under most conditions was greater than the volumes calculated based on freezing-point depression. The equivalent liquid layer thickness, assuming that liquid water is uniformly distributed around the grains, ranged from 3–30 nm at -60°C to 500–3000 nm at -1°C. Corresponding ionic strengths for the two temperatures were 1.7–0.0012 M and 0.005–0.00009 M. Lower values were for ice made from distilled water, and higher values were for ice made from 10<sup>-3</sup> M NaCl. Estimated pH values were from 2.9 at -60°C to 4.1 at -1°C. Results demonstrate that gas absorption can be used to estimate an equivalent liquid volume and thickness for the ice-air interfacial region. While not directly comparable to physical measurements, the estimated values should be directly applicable to modeling uptake of SO<sub>2</sub> and other trace gases by ice. Lack of good thermodynamic data for temperatures below 0°C is the main limitation to applying this method.

### INTRODUCTION

Snow is a porous medium, a mixture of ice, air, and sometimes liquid water. Water can also be present at temperatures below 0°C because of freezing-point depression in the presence of solutes [Adamson, 1979] and surface curvature [Colbeck, 1980]. Essentially all of the liquid water in stable grain clusters (at temperatures at and below 0°C) should be in the veins or fillets because of curvature effects [Colbeck, 1979]. Considerable evidence also suggests that an interfacial region having liquidlike properties or a disordered surface film is also present on one or more faces of the grains [Nenow, 1984]. There is both thermodynamic evidence [Fletcher, 1968; Gubler, 1982] and experimental evidence [Golecki and Jaccard, 1978; Clifford, 1975] to support the existence of such a layer. For example, adsorption of SO<sub>2</sub> onto ice has been observed to increase with temperature from -35°C to near 0°C [Sommerfeld and Lamb, 1986]. It is thought that gas adsorption at these and even lower temperatures is due to trapping of solute molecules at the surface by mobile water molecules (i.e., a surface liquidlike layer) [Ocampo and Klinger, 1982] as the temperature approaches the melt point. This is consistent with the observed increase in surface roughening for crystals grown above about -10°C [Colbeck, 1985].

Gas uptake by snow occurs primarily by dry deposition, because snow on the ground generally has a higher temperature and a much longer exposure time than snow crystals in the atmosphere. For all but the most soluble or reactive gases, dry deposition to snow is determined almost entirely by interactions below the (macroscopic) snowpack surface [Bales, 1991]. Gases are transported into and out of the snowpack by diffusion, wind ventilation, and atmospheric

pressure changes. Absorption and adsorption of these gases at the surface of snow grains, i.e., the ice-air interface, determine the concentrations of gaseous species that accumulate in both seasonal snow and glacial firn.

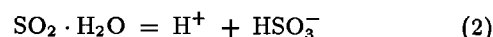
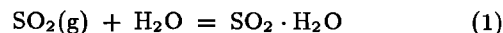
The grain scale distribution of the deposited material is changed by metamorphism, sublimation, and freeze/thaw cycling, but most impurities are excluded from the ice matrix, resulting in their accumulation at the ice-air interface. Even chemical species that are incorporated into snow during formation in clouds or by atmospheric scavenging and riming as snow falls through the atmosphere should move to the ice-air interface because of recrystallization processes continually occurring in the snowpack.

In general, it is the chemical properties of the ice-air interfacial region rather than the bulk snow properties that influence the reactivity of snow. Besides partitioning, reactions such as photolysis and oxidation of HCHO and scavenging of H<sub>2</sub>O<sub>2</sub> are important examples.

The objective of the work reported in this paper was to estimate the equivalent amount of liquid water present at the ice-air interface from information on the uptake of SO<sub>2</sub> onto ice. Experimental results on the uptake of SO<sub>2</sub> onto ice at temperatures from -3 to -60°C were reported by Conklin *et al.* [1993]. The amount of SO<sub>2</sub> accumulated on the ice surface was measured by melting the ice, and allowing the SO<sub>3</sub><sup>2-</sup> to oxidize the SO<sub>4</sub><sup>2-</sup> and measuring the SO<sub>4</sub><sup>2-</sup> on an ion chromatograph.

### MODEL

The chemical system under consideration is that of SO<sub>2</sub> gas in equilibrium with an aqueous NaCl solution. Reactions describing the absorption of SO<sub>2</sub> by liquid water and subsequent dissociation in the aqueous phase are



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There are seven aqueous chemical species to consider in order to define the system: H<sup>+</sup>, OH<sup>-</sup>, SO<sub>2</sub> · H<sub>2</sub>O, HSO<sub>3</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, Na<sup>+</sup>, and Cl<sup>-</sup>.

Mathematical equations defining the system include four mass law expressions

$$[\text{SO}_2 \cdot \text{H}_2\text{O}] = K_H P_{\text{SO}_2} \quad (4)$$

$$K_{a1} = \frac{[\text{H}^+][\text{HSO}_3^-]\gamma_+\gamma_-}{[\text{SO}_2 \cdot \text{H}_2\text{O}]} \quad (5)$$

$$K_{a2} = \frac{[\text{H}^+][\text{SO}_3^{2-}]\gamma_+\gamma_-}{[\text{HSO}_3^-]} \quad (6)$$

$$K_W = [\text{H}^+][\text{OH}^-]\gamma_+\gamma_- \quad (7)$$

where the brackets stand for molar concentration,  $P_{\text{SO}_2}$  stands for partial pressure (atm), and  $\gamma_{\pm}$  is an activity coefficient. There are also three mass conservation equations, for total sulfur ( $S_T$ ), total sodium ( $Na_T$ ), and total chloride ( $Cl_T$ )

$$S_T = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (8)$$

$$Na_T = [\text{Na}^+] \quad (9)$$

$$Cl_T = [\text{Cl}^-] \quad (10)$$

The electroneutrality condition gives an additional equation

$$[\text{H}^+] + [\text{Na}^+] - [\text{OH}^-] - [\text{HSO}_3^-] - 2[\text{SO}_3^{2-}] - 2[\text{Cl}^-] = 0 \quad (11)$$

The activity coefficients for charged species are a function of ionic strength ( $I$ ) and can be calculated from the Davies equation

$$\log_{10} \gamma_{\pm} = -0.5z^2 \left[ \frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right] \quad (12)$$

where  $z$  is the ion's charge number. Note that the constant 0.5 in equation (12) varies slightly with temperature, with values of 0.5116 and 0.4918 reported for 25° and 0°C, respectively [e.g., *Sposito*, 1981]. Linear extrapolation would give a value of 0.4443 for -60°C. For the current analysis, we used 0.5 for all temperatures. Ionic strength is

$$I = 0.5 \left[ [\text{H}^+] + [\text{Na}^+] + [\text{OH}^-] + [\text{HSO}_3^-] + 4[\text{SO}_3^{2-}] \right] \quad (13)$$

For each of the four remaining mass law expressions, values of the equilibrium coefficients are needed at the temperatures of interest. Since values have not been measured

near or below zero, we use available equilibrium constant and enthalpy values for 25°C to estimate constants for lower temperatures (Table 1) using the van't Hoff equation [e.g., *Stumm and Morgan*, 1981].  $P_{\text{SO}_2}$  was 89 parts per billion by volume for all experiments.

The aqueous phase in the experimental system under consideration is at the surface of ice grains, i.e., in the ice-air interfacial region. Experimentally, values of total sulfur, sodium, and chloride were measured for the bulk ice rather than the surface (aqueous) phase. The bulk and surface values differ by a factor, i.e., the fraction of the ice that is liquid ( $f_w$ ). For example, for sulfur, the bulk ( $S_{Tb}$ ) and surface ( $S_T$ ) quantities are related by

$$S_T = \frac{S_{Tb}}{f_w} \quad (14)$$

That is, we explicitly assume that essentially all of the impurities are concentrated at the surface of the ice grains, i.e., at the ice-air interface, and thus are in the surface melt layer.

Substituting equation (14) into (8), making similar substitutions for (9) and (10), and using (12) to calculate the  $\gamma$  values in (5) through (7) leaves nine equations ((4) through (11) and (13)), and nine unknowns. The unknowns are concentrations of seven chemical species,  $I$  and  $f_w$ . The resulting set of nonlinear equations was solved iteratively using the Newton-Raphson method. Calculated results were substituted into the equations to check for consistency.

## RESULTS

The experimental data used in the calculations are summarized in Figure 1. One set of experiments was done with ice made from distilled water, and in two sets the ice was made from NaCl solutions. The concentrations of NaCl used bracket the ionic strengths found in seasonal snowpacks, with 10<sup>-3</sup> M reflecting snow found in areas impacted by anthropogenic pollution and 10<sup>-5</sup> M reflecting snow in pristine environments. It is assumed that in all three sets, there was no oxidation of S(IV) to S(VI). *Conklin et al.* [1993] reported two other sets of experiments in which H<sub>2</sub>O<sub>2</sub> and NaCl were both present in the ice. Total uptake was considerably higher for the ice that was doped with H<sub>2</sub>O<sub>2</sub>, but the relative S(IV) to S(VI) uptake was not measured. No other oxidants were present in the system.

Since SO<sub>2</sub> uptake into a solution without excess base will have a low pH, OH<sup>-</sup> can be neglected, and equation (7) drops out. It is also known that  $\frac{Na_T}{f_w} = \frac{Cl_T}{f_w} = [\text{Na}^+] =$

## TABLES

TABLE 1. Thermodynamic Data

Reaction	Log K		$\Delta H^\circ$ , kJ mol <sup>-1</sup>	Reference
	25°C	0°C		
SO <sub>2</sub> (g) + H <sub>2</sub> O = SO <sub>2</sub> · H <sub>2</sub> O	0.095	0.514*†	-26.13	[ <i>Smith and Martell</i> , 1982]
SO <sub>2</sub> · H <sub>2</sub> O = H <sup>+</sup> + HSO <sub>3</sub> <sup>-</sup>	-1.91	-1.642*	-16.72	[ <i>Smith and Martell</i> , 1982]
HSO <sub>3</sub> <sup>-</sup> = H <sup>+</sup> + SO <sub>3</sub> <sup>2-</sup>	-7.18	-7.318*	-12.5	[ <i>Smith and Martell</i> , 1982]
H <sub>2</sub> O = H <sup>+</sup> + OH <sup>-</sup>	-14.00	-14.93	-†	[ <i>Harned and Owen</i> , 1958]

\*Calculated from  $K$  at 25°C and  $\Delta H^\circ$ .

†Units of molar concentration per atmosphere.

‡Log  $K_w = \frac{-4470.99}{T} + 6.0875 - 0.01706 T$  where  $T$  is in °K.

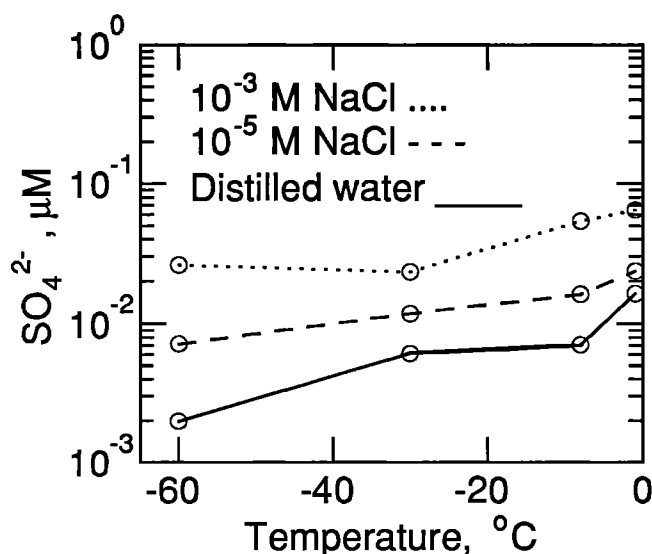


Fig. 1. SO<sub>2</sub> uptake on ice spheres at equilibrium [Conklin *et al.*, 1993]. Mean concentrations reported are for bulk ice. Data are for ice made from three different solutions with no oxidant present.

[Cl<sup>-</sup>]. Making the further assumption that the pH was sufficiently low so that [SO<sub>3</sub><sup>2-</sup>] ≪ [HSO<sub>3</sub><sup>-</sup>] and rearranging gives a smaller set of equations. The electroneutrality condition (11) becomes

$$[H^+] = [HSO_3^-] \quad (15)$$

and the equation for total sulfur (8) is

$$\alpha_0 + \alpha_1 = 1 \quad (16)$$

where the ionization fractions  $\alpha_0$  and  $\alpha_1$  are

$$\alpha_0 \equiv \frac{[SO_2 \cdot H_2O] f_w}{S_{Tb}} = \left[ 1 + \frac{K_{a1}}{[H^+] \gamma_+} + \frac{K_{a1} K_{a2}}{[H^+]^2 \gamma_+^2} \right]^{-1} \quad (17)$$

$$\alpha_1 \equiv \frac{[HSO_3^-] f_w}{S_{Tb}} = \left[ \frac{[H^+] \gamma_+}{K_{a1}} + 1 + \frac{K_{a2}}{[H^+] \gamma_+} \right]^{-1} \quad (18)$$

For low [SO<sub>3</sub><sup>2-</sup>], the terms containing  $K_{a2}$  drop out of the expressions for the  $\alpha$  values. Considering (15), ionic strength is

$$I = 0.5 \left[ 2[H^+] + \frac{Na_T}{f_w} + \frac{Cl_T}{f_w} \right] \quad (19)$$

Substituting the  $\alpha$  values, equations (17) and (18), into (16) gives an equation in only [H<sup>+</sup>] and  $\gamma_{\pm}$

$$\left[ 1 + \frac{K_{a1}}{[H^+] \gamma_+} \right]^{-1} + \left[ \frac{[H^+] \gamma_+}{K_{a1}} + 1 \right]^{-1} = 1 \quad (20)$$

when  $\gamma_{\pm}$  is given by equation (12) and  $I$  is given by (19). To calculate  $I$ , one needs  $f_w$ , which is given by combining equations (14) and (15) with the definition in equation (18)

$$f_w = \frac{\alpha_1 S_{Tb}}{[H^+]} = \frac{S_{Tb}}{[H^+]} \left[ \frac{[H^+] \gamma_+}{K_{a1}} + 1 \right]^{-1} \quad (21)$$

For ice made from distilled water, the  $Na_T$  and  $Cl_T$  terms

drop out of equation (19), and the system composition is simply that of water in equilibrium with SO<sub>2</sub> gas.

The results of the iterative solution are given on Figure 2. The  $f_w$  values show both a strong temperature and ionic-strength dependence (Figure 2a). For all three ice compositions,  $f_w$  drops about 2 orders of magnitude in going from -3 to -60 °C. The  $f_w$  values for ice made from 10<sup>-3</sup> M NaCl are 3–10 times those for ice made from distilled water.

The liquid phase is a brine solution at -60 °C and 10<sup>-3</sup> M NaCl ( $I = 1.7$ ) but has a lower  $I$  at -1 °C (0.005 M in 10<sup>-3</sup> M NaCl versus 0.0009 M in distilled water, Figure 2c). Estimated pH values (-log [H<sup>+</sup>]  $\gamma_+$ ) in the liquid phase range from 2.9 to 4.1 for temperatures of -60 and -1 °C, respectively (Figure 2b). At all temperatures studied, the liquid phase, or equivalent liquid-phase composition, is highly acidic.

The specific surface area of ice spheres prepared and packed by the procedure used in these experiments was reported by Conklin *et al.* [1993] to be near 150 cm<sup>2</sup> cm<sup>-3</sup>. They used stereology to arrive at the estimates. Multiplying  $f_w$  by the volume of ice per column [Conklin *et al.*, 1993] and dividing by the values measured for each experiment gives estimates of the equivalent thickness of a liquid layer distributed uniformly over the surface (Figure 3). Values range from 3 nm at -60 °C with ice made from distilled water to over 1 μm at -3 °C with ice made from 10<sup>-3</sup> M NaCl.

#### DISCUSSION

Liquid water is present in brine solutions at the ice-air interface in snow at temperatures below 0 °C due to freezing-point depression. The relation between ionic composition and freezing point for water is [Adamson, 1979]

$$\Delta T = 1.86 m \quad (22)$$

where  $m$  is molality and  $T$  is temperature. Continuing with the assumption that essentially all ions are excluded from the ice,  $m$  is equal to  $\frac{I}{f_w}$ . In other words, the expected  $f_w$  due to freezing-point depression is

$$f_w = \frac{1.86 I}{\Delta T} \quad (23)$$

where  $I$  values were estimated from the experiments (Figure 2b).

For ice made from distilled water or 10<sup>-5</sup> M NaCl and at temperatures near 0 °C,  $f_w$  values estimated in this manner were about 1–10% of values estimated from the SO<sub>2</sub> experiments. That is, there was more liquid water than could be accounted for by freezing-point depression. At -60 °C, the two estimates were within a factor of 2. We suggest that the greater uptake and thus  $f_w$  estimated from experiments reflect a significant absorption, or hydration, of SO<sub>2</sub> over much of the grain surface in addition to absorption at grain boundaries. At colder temperatures the faces are more faceted and absorption should be significantly lower. At -60 °C, uptake could be largely by adsorption. For ice made from 10<sup>-3</sup> M NaCl,  $f_w$  values estimated from equation (23) were 2 and 100 times those calculated from the experiments at temperatures from -60 to -8 °C, respectively. Underestimates of  $f_w$  with the ice made from 10<sup>-3</sup> M NaCl could be due in part to greater error in estimating  $K_H$  and  $K_{a1}$  for cold brine solutions.

One should carefully consider the assumption that ionic species are largely excluded from the ice matrix. Relatively

few measurements have been made of the distribution coefficient  $K_D$  (solid concentration divided by liquid concentration) for the ice-water system. The equilibrium distribution of alkali metal fluorides and chlorides gives  $K_D$  values on the order of  $10^{-4}$  –  $10^{-3}$  [Gross, 1968, 1977] but depends on counterion concentration. Higher values are reported for NH<sub>4</sub>F (0.13) [Gross *et al.*, 1975], and antifreeze glycoprotein

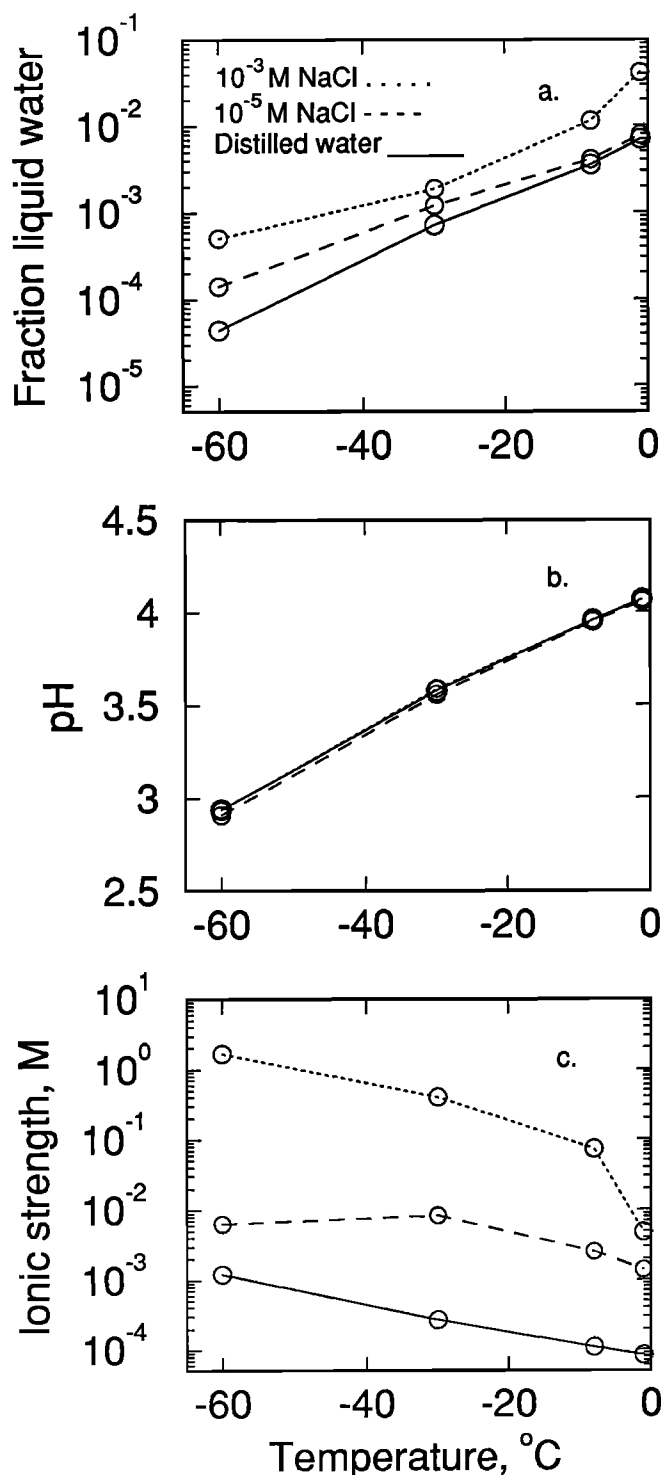


Fig. 2. Estimated average values versus temperature based on equilibrium model and data of Figure 1 for (a) fraction liquid water, (b) pH, and (c) ionic strength for surface region. Lines connecting data are for clarity.

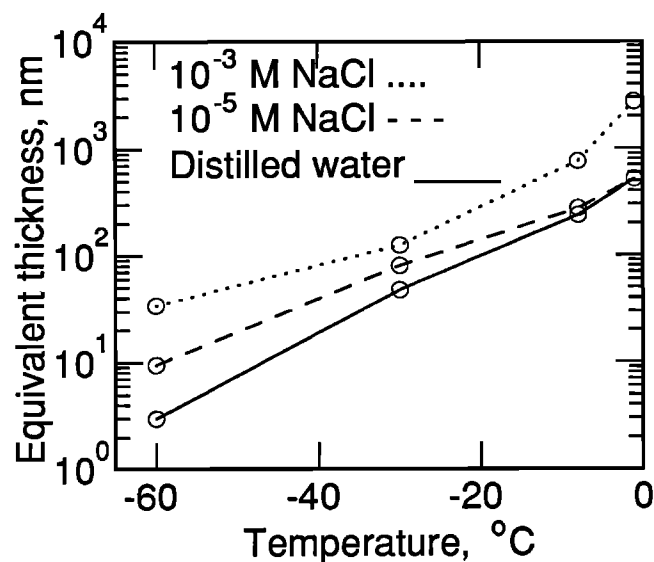


Fig. 3. Equivalent thickness of liquid layer based on uniform distribution around surface of ice sphere; estimated from equilibrium model.

(0.8) [Gross *et al.*, 1987]. In general, measured ice-water partition coefficients for most species are very small. Chemical species such as Na<sup>+</sup>, Cl<sup>-</sup>, HSO<sub>3</sub><sup>-</sup>, and SO<sub>2</sub> · H<sub>2</sub>O (or ion pairs) are relatively large and should not fit well into the ice matrix. So there seems little reason to doubt our assumption that essentially all of the ions are at the ice-air interface.

During rapid formation of ice crystals, impurities should be distributed throughout the grain; slower growth or metamorphism should result in concentration of species near the surface because the presence of an impurity in a crystal lattice causes a strain greater than that caused by its presence on the grain boundary, which is disordered compared to the interior of the crystal. Thus an interaction energy drives solutes in growing crystals toward the boundary. Results in our laboratory suggest that freezing 0.2-mm droplets in liquid N<sub>2</sub> is "slow" and results in polycrystalline ice spheres with only small grain scale concentration gradients [Bales, 1992].

The apparent  $f_w$  values and equivalent liquid thicknesses estimated from SO<sub>2</sub> uptake provide order-of-magnitude values for the amount of liquid water in snow. These estimates are not intended to be directly comparable to physical measures of aqueous films on crystal faces. Rather, they provide a measure of the relative uptake capacity of snow for soluble atmospheric trace gases. For example, they suggest that in seasonal snowpacks, spring snow ( $T \approx 0^\circ\text{C}$ ) has about three or four times the capacity of winter snow ( $T \approx -8^\circ\text{C}$ ) to take up gases such as SO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, organic acids, NH<sub>3</sub>, or O<sub>3</sub>. Snowfall impacted by anthropogenic pollution will have a significantly higher (about an order of magnitude) uptake capacity for soluble gases than snow in pristine areas. Further, uptake of ionic species should facilitate even more uptake owing to the strong ionic strength dependence of  $f_w$ . One exception is that SO<sub>2</sub> uptake lowers pH, which would reduce further uptake of acids that dissociate [Bales *et al.*, 1987]. In fact, low pH values associated with SO<sub>2</sub> uptake could result in degassing of weaker acids. NH<sub>3</sub> absorption would buffer the system.

At the much colder temperatures of polar ice ( $T \approx -30^\circ\text{C}$ ), gaseous uptake should be significantly lower than in seasonal snow, owing to the nearly 10-fold difference in  $f_w$ . Polar snow (and high alpine snow) generally has a lower ionic content than does seasonal snow, which also suggests a low  $f_w$  and a low capacity for absorption of gases.

#### CONCLUSIONS

Our calculations suggest that the mass fraction of liquid water and thus equivalent liquid thickness at the ice-air interface depend strongly on the ionic content of the ice. The  $f_w$  value at  $-60^\circ\text{C}$  was only 1% of that for  $-3^\circ\text{C}$ . Uptake of trace gases, such as SO<sub>2</sub>, from the atmosphere results in an increase in the volume of this surface phase.

Gas adsorption/absorption provides a novel way to estimate the equivalent volume of liquid water present at the ice-air interface. Estimates made in this manner should be more directly applicable to chemical modeling of trace gas-ice interactions than estimates made by physical or spectroscopic methods. The two main uncertainties with our calculations are the assumption that no oxidation of S(IV)  $\rightarrow$  S(VI) occurs on the ice surface, and the extrapolation of Henry's coefficients and acid dissociation constants to low temperatures.

At temperatures near freezing, the amount of SO<sub>2</sub> (ab)sorbed by ice was greater than could be accounted for by assuming equilibrium between air and an aqueous phase with a volume determined by freezing-point depression. This deviation may be due to the assumption that no oxidation occurred on the ice surface. At lower temperatures and with salts initially present in the ice, experimental estimates converged to those calculated from freezing-point depression.

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