

# Measurement of the Specific Surface Area of Snow with the Nitrogen Adsorption Technique

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Few data exist for the surface area of snow despite its importance for modeling wet deposition and migration of reversibly deposited contaminants in snow. A method for determining the surface area of snow is described that uses a commercial nitrogen adsorption instrument (Gemini III 2375, Micromeritics Instruments Inc.). The method uses a sample vial containing snow and a reference vial containing an equal amount of snow that has been melted and refrozen in order to minimize its surface area. The basic quantity measured is the difference in volumes of nitrogen delivered to the sample and reference vials. This volume difference must be corrected for the free space difference in the vials before the adsorbed volume of nitrogen can be inferred. Two methods for obtaining this correction are discussed, measured, and estimated, and the results of BET analysis are presented for both types of correction. Fresh snow samples collected in southern Ontario exhibit type II isotherms with moderate to small BET constant values. Snow surface area ranges from 0.06 to 0.37 m<sup>2</sup>/g. Comparison with literature data for the dimensions of snow crystals suggests that the BET surface area of snow is comparable to the surface area measured by microscopy techniques.

## Introduction

Snow crystals have been extensively photographed (1) and classified (2), and the morphology of snow has been related to meteorological parameters (2, 3), but there have been few measurements or estimates of the surface area (SA) of snow.

Due to the large SA of snow relative to rain and the very small diffusion coefficients for solutes in ice relative to liquid water, snow SA may be an important parameter for quantifying the removal of gaseous constituents from the atmosphere by falling snowflakes.

Snow SA is needed for modeling the scavenging by snow of nonpolar organic vapors, because they are removed by physical adsorption on the snow crystal surfaces rather than by dissolution in the ice lattice. The gaseous scavenging efficiency  $W_g$  is the volume of air extracted by a unit volume of precipitation.  $W_g$  is operationally defined as  $C_p/C_a$ , where  $C_p$  and  $C_a$  are the concentrations (mol/m<sup>3</sup>) in precipitation and air, respectively. Both concentrations are measured at ground level where the precipitation is collected. Assuming the hydrometeor is in equilibrium with the chemical vapor in the atmosphere,  $W_g$  can be estimated for rain as  $K_{wa}$  and for snow as  $K_{ia}A_s\rho$ . In these expressions,  $K_{wa}$  (dimensionless) is the Henry's law partition coefficient for water,  $K_{ia}$  (m) is the adsorption coefficient for ice,  $A_s$  (m<sup>2</sup>/g) is the specific surface area of the snow, and  $\rho$  (g/m<sup>3</sup>) is the density of the snowmelt water (4). Adsorption coefficients for nonpolar organic chemicals at the air–water interface were compiled, and a method for correlating them was given (5). Experimental evidence was presented showing that to a first approximation, the adsorption coefficients for ice can be estimated by extrapolating the values for water to lower temperature (6). Snow SA is also needed for quantifying the distribution of nonpolar organic chemicals in snow deposits. Because SA decreases slowly as the snow ages, there is a tendency for the chemicals to redistribute in the snow deposit and to diffuse out of it (7). This process can affect the concentrations of nonpolar organic chemicals in snowmelt water and in glacial ice.

The development of convenient and reliable methods for determining snow SA would further two objectives: (i) determining the magnitude and variability of the SA of freshly precipitated snow and its relation to meteorological factors and (ii) determining the temperature-dependent rate of decrease of snow SA during metamorphosis. The BET nitrogen adsorption technique is commonly used to determine surface area for a wide variety of materials, but it is not easily applied to snow. The main problem seems to be that snow has a surface area to volume ratio of the order 10<sup>4</sup> m<sup>-1</sup>, which is close to the lower limit of quantification for the nitrogen adsorption technique. We describe here a method for measuring the SA of snow using a commercial surface area analyzer, and we present results for fresh snow samples collected in southern Ontario.

## Experimental Methods

**Sampling and Analysis.** The specific surface area of the snow samples was determined with a Gemini III 2375 surface area analyzer (Micromeritics Instruments Corp.). This instrument measures the difference in the volumes of nitrogen delivered to a sample vial and a reference vial. The sample vial contains the material whose surface area is to be determined, and the reference vial contains an inert (low surface area) material that displaces an approximately equal volume of gas. The vials are immersed to the same level in liquid nitrogen, and they are held at the same pressure during the measurement. The measurement of a differential volume thus compensates for changing temperature gradients in the sample vial.

Six snow samples were collected in January and February of 1995 at the University of Waterloo, Waterloo, ON. The snow was taken from several centimeter thick deposits,

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usually within a few hours of falling, at temperatures below freezing. Approximately equal quantities ( $\sim 6 \text{ cm}^3$ ) of snow were placed into the sample and reference vials. We used the bulb-shaped  $12 \text{ cm}^3$  glass vials for materials having small SA (8). The vials were closed with rubber stoppers and kept in a dewar of dry ice for a period of about 1 h before determining the SA. This is considered to be a safe storage temperature for that period of time (9). Due to its cohesiveness, snow could not be poured into the vials through a funnel, so the vials were filled in the following manner. Snow was scooped from the deposit into a plastic-coated drinking cup with a plastic spoon. The snow in the cup was settled and then cored with a plastic drinking straw (8 mm od). The snow was pushed out of the straw and into the vial with a plunger made from glass tubing. To avoid altering the SA, the glass vial and plunger were precooled in the dewar of dry ice. The snow was gently settled after each addition by tapping the vial on a solid surface.

The dewar containing the vials of snow was brought into the laboratory, and the reference vial was removed and placed in a beaker of warm water until the snow inside it had melted completely. The melted snow was then refrozen by placing the vial back into the dewar. This procedure destroyed the surface area of the snow in the reference vial while conserving the mass of water. The sample and reference vials were then attached to the instrument ports in a vertical position, and a dewar of liquid nitrogen was brought up so that the snow/ice-filled portions of the vials were completely immersed. This was done very quickly to minimize exposure of the vials to room temperature.

The dewar of liquid nitrogen was manually held in place while the vials were being evacuated. When a pressure of  $\sim 2 \text{ Pa}$  was attained, the dewar platform rose, and the ensuing measurements were performed automatically. Nitrogen was delivered to the vials while maintaining the pressure balance by means of servo valves connected to a differential pressure transducer. The excess quantity of nitrogen delivered to the sample vial,  $V_i^{\text{meas}}$  ( $\text{m}^3 \text{ STP}$ ), was measured at the following relative pressures: 0.01, 0.03, 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, and 0.70. The relative pressure  $X_i$  is equal to  $P_i/P^{\text{sat}}$ , where  $P_i$  (Pa) is the absolute pressure and  $P^{\text{sat}}$  (Pa) is the saturation pressure. The saturation pressure was determined by the procedure given in the instrument manual (8) prior to collecting the snow sample. With an equilibration time of 5 s, an analysis cycle took approximately 35 min to complete. A table of  $X_i$  and  $V_i^{\text{meas}}$  values was printed for each analysis cycle, which was usually repeated several times for each snow sample.

After obtaining the tables of  $X_i$  and  $V_i^{\text{meas}}$  values as described above, the sample vial was removed from the instrument and subjected to the same melting and refreezing treatment that had been applied to the reference vial. The sample vial was then re-installed on the instrument, and several additional analysis cycles were run. After this second set of analysis cycles, the vials were removed from the instrument, and the masses of water were determined by weighing the vials on a platform balance. The data obtained from the second set of analysis cycles were used to correct the data obtained from the first set for the free space difference in the vials as described in the next section.

**Data Reduction.** The BET surface area  $A_{\text{BET}}$  ( $\text{m}^2/\text{g}$ ) was obtained by fitting data for the quantity of nitrogen adsorbed  $V_i^{\text{ads}}$  ( $\text{m}^3 \text{ STP}$ ) at relative pressure  $X_i$  (dimensionless) to the BET equation:

$$X_i / \{V_i^{\text{ads}}(1 - X_i)\} = aX_i + b \quad (1)$$

The slope  $a$  ( $\text{m}^3 \text{ STP})^{-1}$  and intercept  $b$  ( $\text{m}^3 \text{ STP})^{-1}$  were obtained by regression using data points for  $0.03 \leq X_i \leq 0.30$ .  $A_{\text{BET}}$  was then calculated by

$$A_{\text{BET}} = A_m / \{V_m(a + b)W\} \quad (2)$$

where  $A_m$  ( $9.76 \times 10^4 \text{ m}^2$ ) is the molar surface area for nitrogen,  $V_m$  ( $0.02241 \text{ m}^3 \text{ STP}$ ) is the molar volume of an ideal gas, and  $W$  (g) is the mass of snow in the sample vial. The BET constant  $C_{\text{BET}}$  (dimensionless) was calculated by

$$C_{\text{BET}} = (a + b)/b \quad (3)$$

The quantity of nitrogen adsorbed  $V_i^{\text{ads}}$  was obtained by correcting  $V_i^{\text{meas}}$  for the free space difference in the vials and the effect of gas phase non-ideality. The quantity of nitrogen adsorbed is given by

$$V_i^{\text{ads}} = V_i^{\text{meas}} - V_i^{\text{cor}} \quad (4)$$

where  $V_i^{\text{cor}}$  ( $\text{m}^3 \text{ STP}$ ) is the free space correction volume. The free space correction volume can be determined with helium, which is not appreciably adsorbed at liquid nitrogen temperature. However, some controversy exists as to whether errors are caused by diffusion of helium into the ice lattice (10–12). Therefore, two alternative methods of performing the free space correction, 'measured' and 'estimated', were used.

In the measured free space correction method,  $V_i^{\text{cor}}$  was taken as the differential quantity of nitrogen  $V_i^{\text{meas}}$  for the second set of analysis cycles, which was obtained after the snow in both vials had been melted and refrozen. Implicit in this method is the assumption that the density of ice, and hence the free space difference, is not changed by melting and refreezing the snow in the sample vial.

In the estimated free space correction method,  $V_i^{\text{cor}}$  was estimated from the empty volumes of the vials and the masses of ice that were placed in the vials.  $V_i^{\text{cor}}$  was calculated by

$$V_i^{\text{cor}} = C_f^{\text{est}} P_i (1 + P_i C_n) \quad (5)$$

where  $P_i$  (Pa) is the absolute pressure, and  $C_n$  ( $4.94 \times 10^{-7}/\text{Pa}$ ) is the correction factor for gas phase non-ideality (8). The estimated free space correction factor  $C_f^{\text{est}}$  ( $\text{m}^3 \text{ STP}/\text{Pa}$ ) was calculated by

$$C_f^{\text{est}} = (V^{\text{sys}} - V^{\text{ice}}) / (1.013 \times 10^5 \text{ Pa}) \quad (6)$$

where  $V^{\text{sys}}$  ( $\text{m}^3 \text{ STP}$ ) is the system volume correction, and  $V^{\text{ice}}$  ( $\text{m}^3 \text{ STP}$ ) is the quantity of gas displaced by ice at liquid nitrogen temperature and standard pressure.  $V^{\text{sys}}$  was calculated by

$$V^{\text{sys}} = (V^{\text{sam}} - V^{\text{ref}}) (273.13/77.15) \quad (7)$$

where  $V^{\text{sam}}$  and  $V^{\text{ref}}$  ( $\text{m}^3$ ) were determined by weighing the quantities of water needed to fill the sample and reference vials, respectively.  $V^{\text{ice}}$  was calculated by

$$V^{\text{ice}} = \{(M^{\text{ice, sam}} - M^{\text{ice, ref}}) / D^{\text{ice}}\} (273.13/77.15) \quad (8)$$

where  $M^{\text{ice, sam}}$  and  $M^{\text{ice, ref}}$  (g) are the masses of ice in the sample and reference vials, respectively, and

$$D^{\text{ice}} (= 9.25 \times 10^5 \text{ g}/\text{m}^3)$$

is the density of water ice at liquid nitrogen temperature (13). Note that a measured free space correction factor  $C_f^{\text{meas}}$  can be calculated by regressing  $V_i^{\text{meas}}$  obtained from the second set of analysis cycles on  $P_i(1 + C_n P_i)$  while constraining the intercept of the regression line to be zero.

## Results and Discussion

A typical adsorption isotherm is shown in Figure 1. The isotherms had the BET type II shape and exhibited a small

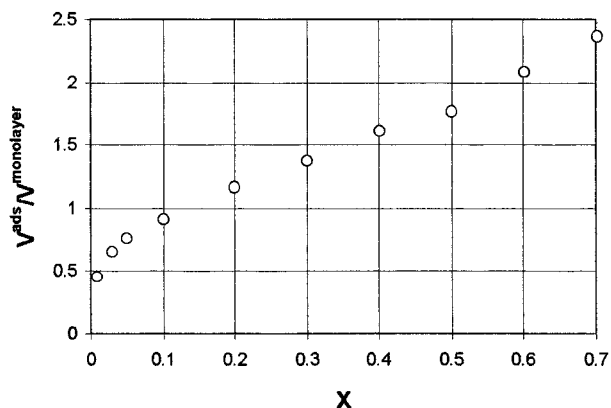


FIGURE 1. Plot of a typical adsorption isotherm for nitrogen on snow.  $V^{\text{ads}}$  ( $\text{m}^3$  STP) is the quantity of nitrogen adsorbed,  $V^{\text{monolayer}}$  ( $\text{m}^3$  STP) is the quantity of nitrogen corresponding to a monolayer, and  $X$  (dimensionless) is the relative pressure of nitrogen.

to moderate amount of curvature in region of monolayer formation ( $0 < X_i < 0.3$ ). This is consistent with the small to moderate values of  $C_{\text{BET}}$  obtained from the BET analysis. Equation 1 provided a good fit to the data in the monolayer region of the isotherm. The BET plots were linear, and the  $R^2$  values for the regressions were greater than or equal to 0.99.

The values of  $C_f$ ,  $A_{\text{BET}}$ , and  $C_{\text{BET}}$  obtained using the two free space correction methods are given in Table 1. The estimated free space correction method usually gave the larger  $C_f$  values. The magnitude of the error ( $C_f^{\text{estd}} - C_f^{\text{meas}}$ ) in units of  $10^{-12}$   $\text{m}^3$  STP/Pa ranged from 0.1 to 3.1 with a root mean square of 1.6. Errors of this magnitude were obtained from error propagation calculations when reasonable assumptions were made about the magnitudes of the errors in  $V^{\text{sys}}$  and  $V^{\text{ce}}$ . For example, errors of  $0.03 \text{ cm}^3$  in  $V^{\text{sys}}$  and  $V^{\text{ce}}$  result in an error of  $2 \times 10^{-12}$   $\text{m}^3$  STP/Pa in  $C_f$ . The fact that ( $C_f^{\text{estd}} - C_f^{\text{meas}}$ ) was usually positive suggests that the errors in  $V^{\text{sys}}$  and  $V^{\text{ce}}$  are systematic.

The  $A_{\text{BET}}$  values in Table 1 are averages of one to four values for each sample. The number of values averaged for each sample are also given in the table. There are 8 degrees of freedom for the replicate determinations, and the pooled relative standard deviation is 9%. The 95% confidence

interval for  $A_{\text{BET}}$ , calculated by error propagation formulas from the standard errors for the slopes and intercepts of the regressions, ranged from 8% to 27%. The estimated free space correction method gave negative values of  $C_{\text{BET}}$  for two samples, and the 95% confidence interval for these samples was unusually large. Therefore, the measured free space correction method is preferred. The range of  $C_{\text{BET}}$  values obtained for the measured method (8–48) is similar to that observed for adsorption of nitrogen on molecular solids (e.g., solid benzene) (14–17), whereas larger  $C_{\text{BET}}$  values are usually observed for refractory materials (e.g., metal oxides). The magnitude of  $C_{\text{BET}}$  reflects the energy of adsorption relative to that of condensation. Snow thus has a relatively low energy surface for adsorption of nitrogen.

The main sources of error in the determination of  $A_{\text{BET}}$  are apparently random error in  $V_i^{\text{meas}}$  and systematic error in the free space difference. The effects of these two kinds of error were investigated by mathematical techniques. The Monte Carlo technique was used to investigate the effect of random errors in  $V_i^{\text{meas}}$ . Experimental data were simulated using typical values for  $WA_{\text{BET}}$  ( $0.5 \text{ m}^2$ ) and  $C_{\text{BET}}$  (15.0). The slope and intercept of the BET equation were calculated by inverting eqs 2 and 3, and the values of  $V_i^{\text{ads}}$  were calculated for  $X_i$  values between 0.03 and 0.30 by inverting eq 1. The values of  $V_i^{\text{meas}}$  were then calculated by adding random errors to  $V_i^{\text{ads}}$  while neglecting  $V_i^{\text{cor}}$ . The random errors were assumed to have a normal distribution and a variance given by benchmark tests performed by Micromeritics. These tests indicate that the standard deviation for  $V_i^{\text{meas}}$  ranges from  $6 \times 10^{-9}$   $\text{m}^3$  STP at  $X_i = 0.0$  to  $2 \times 10^{-8}$   $\text{m}^3$  STP at  $X_i = 1.0$  (18). The experimental data for 250 analyses were thus simulated, and values for  $A_{\text{BET}}$  and  $C_{\text{BET}}$  were calculated for each analysis by regression. The relative standard deviations for  $A_{\text{BET}}$  and  $C_{\text{BET}}$  were 9% and 27%, respectively. Increasing the number of fitted points from 5 to 7 resulted in slightly improved precision.

The following procedure was used to investigate the effect of systematic errors in the free space difference. The values of  $V_i^{\text{ads}}$  were calculated for  $X_i$  between 0.03 and 0.30 by inverting eqs 1–3 as described in the previous paragraph. The values of  $V_i^{\text{meas}}$  were then calculated by inverting eq 4. The values of  $V_i^{\text{cor}}$  were calculated by eq 5 for the range of ( $C_f^{\text{estd}} - C_f^{\text{meas}}$ ) values given in Table 1. The values of  $A_{\text{BET}}$  and  $C_{\text{BET}}$  were then obtained by regression. It was observed

TABLE 1. Sampling Data and Results for  $C_f$  ( $10^{-12}$   $\text{m}^3$  STP/Pa),  $A_{\text{BET}}$  ( $\text{m}^2/\text{g}$ ), and  $C_{\text{BET}}$  (dimensionless) Obtained Using Two Methods of Free Space Correction

	sample no.					
	1	2	3	4	5	6
sampling date	1/2/95	1/2/95	1/3/95	2/15/95	2/21/95	2/24/95
temp on day of sampling ( $^{\circ}\text{C}$ )						
min	-8.5	-8.5	-9.0	-17.4	-11.0	-9.3
max	-5.0	-5.0	-5.3	3.5	0.8	-2.0
snowfall (cm)						
on sampling day	1.8	1.8	3.6	0.2	1.4	0.8
on previous day	3.8	3.8	1.8	1.2	1.0	1.4
mass of snow (g)						
in sample vial	2.67	3.49	3.35	3.03	2.16	1.37
in reference vial	3.87	2.73	3.52	2.88	3.52	2.23
results obtained using estimated free space correction method						
$C_f^{\text{estd}}$	47	-27	8	-4	53	34
$A_{\text{BET}}$	0.07	0.13	0.16	0.06	0.15	0.11
$C_{\text{BET}}$	-184	25	18	38	12	-99
results obtained using measured free space correction method						
$C_f^{\text{meas}}$	46	-27	8	-7	52	31
$A_{\text{BET}}$	0.12	0.13	0.17	0.15	0.15	0.37
$C_{\text{BET}}$	48	26	19	8	12	17
no. of values averaged <sup>a</sup>	1	1	3	4	2	3

<sup>a</sup> The number of values averaged refers to the number of analysis cycles that were used to obtain  $A_{\text{BET}}$  and  $C_{\text{BET}}$ .

that the error in  $A_{\text{BET}}$  was proportional to that in  $C_f$ . The relative error in  $A_{\text{BET}}$  was 55% at  $C_f = 2.25 \times 10^{-12} \text{ m}^3 \text{ STP/Pa}$ . However, the fit to the BET equation was not seriously degraded by an error of this magnitude ( $R^2 = 0.99$ ). The sensitivity of  $A_{\text{BET}}$  to error in  $C_f$  seems related to the smallness of the values of  $A_{\text{BET}}$ ,  $C_{\text{BET}}$ , and the bulk density of snow, which results in a free space difference that is large relative to the differential quantity of nitrogen adsorbed. At pressures corresponding to monolayer coverage, the ratio  $V^{\text{cor}}/V^{\text{ads}}$  ranged from 1.1 to 16.7 for the six snow samples.

This analysis suggests that the uncertainty in the magnitude of  $C_f$  is probably the main factor limiting accuracy in the determination of snow SA by the present method. It is thought that greater accuracy might be achieved by using larger vials containing larger quantities of snow and by minimizing the free space difference in the vials. Further experimental work is also required to evaluate the accuracy of the various free space correction methods.

Our results can be compared with previously reported data for snow SA. Adamson et al. (14) reported a value of  $0.2 \text{ m}^2/\text{g}$  for a sample taken from a blizzard at 8000 ft on Mount Gorgonio near Los Angeles, CA. Adamson et al. (14) also reported a value of  $1.3 \text{ m}^2/\text{g}$  for a day-old sample taken from a field near Denver, CO, whereas Adamson and Dormant (15) gave a value of  $0.4 \text{ m}^2/\text{g}$  for the Denver snow. Jellinek and Ibrahim (9) reported a rather high value of  $7.77 \text{ m}^2/\text{g}$  for an unspecified sample of snow. In these older studies, helium was used to determine the free space correction, and very small values ( $<3$ ) were obtained for  $C_{\text{BET}}$ . Gregg and Sing (19) reported that unreliable surface areas may be obtained when the BET procedure is applied to isotherms having  $C_{\text{BET}}$  values less than 3. In comparison with the previously reported data, our  $C_{\text{BET}}$  values are larger and our  $A_{\text{BET}}$  values are smaller and less variable.

The snow surface areas obtained in this study are considerably smaller than those reported for synthetic ices used to study stratospheric clouds. These ices, which were formed by depositing water vapor on very cold ( $-188 \text{ }^\circ\text{C}$ ) surfaces, had BET areas between  $200$  and  $400 \text{ m}^2/\text{g}$  (12, 20–23). Such large surface areas suggest the existence of micropores (diameter smaller than  $2 \text{ nm}$ ). When the ices were annealed at temperatures between  $-63$  and  $-43 \text{ }^\circ\text{C}$ , surface areas between  $0.2$  and  $1.5 \text{ m}^2/\text{g}$  were observed. These smaller BET surface areas were found to be consistent with the external surface areas of the ice particles as determined by scanning electron microscopy (12, 23). Thus it appears unlikely that snow SA would exceed  $1.5 \text{ m}^2/\text{g}$ .

The SA of snow can be crudely estimated from the dimensions of snow crystals using simple geometrical formulas if one assumes that snow crystals do not have internal porosity. Hobbs (13) and Pruppacher (24) have reviewed data for the dimensions of snow crystals obtained by microscopy techniques. It can be inferred from these data that individual snow crystals range from  $0.03$  to  $0.80 \text{ m}^2/\text{g}$ , and median values for particle size distributions are close to  $0.1 \text{ m}^2/\text{g}$ . Scanning electron microscope (SEM) images of snow crystals have recently been published (25, 26). The SEM images show crystals having dimensions similar to those revealed in the light microscope images. The fuzzy coatings sometimes seen on the edges of snow crystals (26) suggest an upper limit of  $1.0 \text{ m}^2/\text{g}$  for snow SA. Size distributions for cloud droplets, which are relevant for rimed snow, give surface areas ranging from  $0.12$  to  $0.60 \text{ m}^2/\text{g}$  (24). The comparability of the BET areas obtained in the present study with surface areas estimated by light and scanning electron microscopy suggests that the BET technique measures the SA that is visible in the microscope images.

Our BET results, viewed in the context of the previous studies of snow and synthetic ice, provide a basis for speculating about the magnitude of snow SA. We think that

the SA of fresh snow occurring at mid-latitudes is probably between  $0.05$  and  $0.50 \text{ m}^2/\text{g}$ ; surface areas larger than  $1.0 \text{ m}^2/\text{g}$  appear unlikely. More BET measurements are obviously needed to better define the SA of fresh snow, particularly as it is affected by climatic and meteorological conditions. To our knowledge, there has not been any SA measurements for snow occurring in the colder, drier polar regions. More work is also needed to define the rate at which snow SA decreases as a function of the initial SA and the temperature.

We believe that snow SA is needed for modeling the behavior of semivolatile nonpolar organic compounds in the atmosphere and in snow deposits. For example, the higher  $n$ -alkanes have small vapor pressures and small water/air Henry's law constants. Adsorption is significant while bulk partitioning is negligible. The adsorption coefficients and snow SA should determine the scavenging ratios for  $n$ -alkanes. In contrast, acidic gases (e.g., HCl and  $\text{HNO}_3$ ) have large vapor pressures, and their effective water/air Henry's law constants are 12 orders of magnitude larger than those for  $n$ -alkanes. It is believed that nitric acid is co-condensed with water vapor in snow-forming clouds. Its scavenging ratio should be determined by its air/ice partition coefficient or by collision kinetics (27). Although snow SA may be superfluous for scavenging of acidic gases, it may still be needed to explain the concentrations in snow deposits. That is because the concentrations may change after deposition due to exchange with the atmosphere (28). The mass transfer rates for this process are dependent on air/ice partition coefficients, diffusion coefficients in ice, and snow SA (29). Snow SA may thus be needed for interpreting the concentrations in glaciers of nonpolar and polar atmospheric constituents.

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