Morphology and Surface Areas of Thin Ice Films

Ming-Taun Leu*, Leon F. Keyser, and Raimo S. Timonen
Earth and Space Sciences Division, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California 91109

Abstract

Thin ice films formed by deposition from the vapor phase in a fast flow-tube reactor have been used to simulate polar stratospheric cloud surfaces in order to obtain laboratory data on uptake and heterogeneous reaction rates. Environmental scanning electron microscopy is used to obtain particle sizes and shapes, and to investigate morphology of the ices prepared on borosilicate substrates. Surface areas are determined from BET (Brunauer, Emmett, and Teller) analysis of gas adsorption isotherms. The results for ices prepared at 196 K or 77 K are consistent with previous data obtained by using thicker ice films prepared in a separate apparatus. The uptake of HCl in ice films prepared at 196 K using the same flow-tube reactor is also measured to be approximately 1×10^{14} molecules/cm^2 when a partial pressure of HCl about 5×10^{-7} Torr is used.

* Author to whom the correspondence should be addressed.
(microsoft word-ice].doc; 8/6/96)

Introduction

The loss of ozone in the Antarctic stratosphere is well known to be initiated by heterogeneous reactions occurring cm the suf-face of ice clouds that form when temperatures drop during the winter [1 ,2], in the laborat my the icc clouds have been simulated by condensing the vapors onto cold substrates, for example, borosilicate glasses and silicon. The resulting icc films have been used to obtain HCl uptake parameters [3-5] and reaction probabilities for the following reactions [6-11]

$ClONO_2 + 11_20 \rightarrow HNO_3 + I1OC1$ (1)

$ClONO_2 + HCl \rightarrow HNO_3 + Cl_2$ (2)

$HOCl + HCl \rightarrow Cl_2 + H_2O$ (3)

$N_2O_5 + H_2O \rightarrow 2\ HNO_3$ (4)

$N_2O_5 + HCl \rightarrow ClNO_2 + HNO_3$ (5)

In order to usc these probabilit ics in atmospheric models, wc need to know the area of the film surface that actually participates in the reaction. It is important 10 know not only the total surface area but also the film morphology in order to determine where and how the surface is situated and, thus, what fraction of surface is available for uptake or reaction.

Total surface area measurements have been reported [12] for nonuniform ice films prepared in a separate apparatus with thicknesses 12^0- 540 µm. Preliminary results on the morphology of ice films investigated by environmental 'scanning electron microscopy (ESEM) has been published.[13] in this article wc report *in-situ* measurements of icc surface area and HCl uptake. Also, a detailed study of the morphology of ice films using *1* ESEM and a micromanipulator is discussed.

Experimental Methods

Morphology Measurements

The morphology of ice films was investigated by using ESEM. A schematic of the apparatus is shown in Figure 1. Icc films were formed by passing a mixture of H_2O vapor and nitrogen over polished borosilicate, silicon or aluminum plates which were cooled to about 77-190 K. Total pressure was about 2.0 Torr with H_2O vapor partial pressures near 0.04 Torr. The silicon plate was extremely smooth; surface irregularities such as cracks or pits were smaller than 0.1 pm, the highest resolution at which the microsope was operated, However, the surfaces of the aluminum and borosilicate plates were found to have hairline cracks and/or machining tool marks. As discussed below, the smoothness of these plates affects the morphology of icc films. A micromanipulator was used to remove

some of the large ice granules situated at the top of the ice film so that the internal packing structure of these films could be observed.

Surface Area Measurements

A U-shaped fast-flow reactor (Figure 2) was used to measure sul-face areas of ice films deposited from water vapor in a helium carrier using a sliding injector. The reactor was made of borosilicate tubing 40 cm in length and 2.50 cm inside diameter. The injector, also made of borosilicate tubing, was 100 cm in length and 1.25 cm outside diameter; it was heated by passing a large flow of nitrogen gas through an outside jacket in order to prevent ice condensation inside the injector. The ice film was prepared by moving the injector from the bottom to the top of the flow tube. Temperature was measured by using a pair of thermocouples attached to the wall. In this study either a solid CO_2 plus methanol slurry or liquid nitrogen was used as a refrigerant. Flow rates of water vapor in helium were controlled by using a stainless steel needle valve and read on a 1 Iastings mass flowmeter. The mass of ice deposited in the flow reactor was calculated from the flow rate and the duration of deposition. The thickness, h, of ice films ranged from 1.04 to 47.4 pm and was calculated from the mass, M; the underlying geometric area of the flow tube, Ageom; and the bulk density, $\rho_b = 0.63$ g/cm^3; $h = M / (\rho_b A_{geom})$. [12

1

Surface areas were measured by using the Brunauer, Emmett, and Teller (BET) method to analyze adsorption isotherms obtained at a temperature of 77 K.[14] The U-tube was submerged in liquid nitrogen and isotherms were determined volumetrically by expanding from a calibrated volume of 519.6 cm^3 maintained at room temperature. The adsorptive gas used in these experiments was Kr. The saturation pressure (P_o) of Kr was measured to be 1.70 '1'err, which agrees exactly with the literature value for the vapor pressure of the solid at 77 K. [15] A value of 20.2 A^2 was used as the average area occupied by Kr atoms on the surface [16,17]. The pressure measurements were corrected for thermal transpiration between the cold adsorption cell and the room tempreature section of the apparatus. Non-ideal gas corrections were negligible. The surface area measurements were corrected for the surface area of the blank cell, which was determined in a separate experiment. The error of these measurements was estimated to be about ± 100 cm^2.

HCl Uptake Measurements

The uptake of HCl in water ice was investigated in the same flow-tube reactor interfaced with a differentially pumped quadruple mass spectrometer. HCl-He mixtures were prepared by mixing HCl (Matheson semiconductor-purity, 99.995°/0) and 1 le (Matheson-purity, 99.9999%) in a glass manifold which was previously evacuated to less

than 1 0^{-6} Torr. Flow rates of the mixture were monitored by a 1 lastings mass flowmeter At first the HCl-He mixture was admitted to the flow reactor through an inlet located at the downstream end; this bypassed the ice film and allowed the vacuum lines to be conditioned with HCl. At the start ofa typical uptake measurement, the flow was redirected through another inlet at the upstream end of the ice film.

Results and Discussion

Morphology Measurements

The morphology of ice films deposited cm a borosilicate plate at 190 K is shown in Figure 3. in the top-view panel a micromanipulator was used to remove a large icc granule in order to make the underlying structure clearly discernible. in the side-view pane] the thickness of ice film can bc measured; again, the layered packing is evident,

A silicon plate was also examined by the ESEM; no cracks, scratches, or pits wet-c discernible. Water ice deposited on this plate exhibited nearly perfect hexagonally shaped crystals which were surrounded by much smaller crystals (d < 1 pm), This is in contrast to the data obtained for the ice films deposited on a borosilicate plate as shown in Figure 3.

We have also performed some experiments by depositing ice films on borosilicate or silicon plates at 93 K. By using a resolution of about O. 1 μm, wc find that the films are comprised of very small amorphous particles (not crystalline). Moreover, as discussed in a previous article [12] micropores maybe present inside the particles at this temperature.

Surface Area Measurements

1. Ice films deposited at 77 K.

In order to compare the results for ice films deposited at warmer temperatures, we performed some experiments at 77 K. A typical BET plot of these experiments is shown in Figure 4. The ice film was formed over a period of40 min by moving the injector from the bottom to the top of onc arm of the U-shaped flow tube shown in Figure 2. The tip of the injector was about 0.5 cm above the liquid nitrogen level, which was raised as the injector was moved upward. The length of the flow reactor covered by ice was about 20 cm. The mass of icc was 63.9 mg and the thickness was 5.78 μm. The BET plot is linear over a relative pressure (P/Po) range, 0.05- 0.4; this is typical of many BET plots and implies that nitrogen adsorption on these ice films is well behaved. The ratio of the ice surface area to the geometric area of the underlying flow tube was calculated to be 928 and the specific surface area was determined to be 256.2 m^2/g.

Wc also perfomed a series of expel-imcnts by varying the mass from 19.7 to 119.1 mg (thickness =1.78 to 10.8 μm). The results arc summarized in Table 1. The ratio of the ice surface area to the geometric area, increases from 305 at a thickness of 1,78 um to

an average of about 2500 at 10.8 um. The increase in this ratio with thickness was also observed for ice films at 196 K (see below). The specific surface area was also calculated and the results are shown in '1'able 1. The specific sur-face area is independent of the thickness within experimental error; this differs from ice deposited at 196 K and suggests that the morphology of ice films formed at the two temperatures may be significantly different (see below). The specific surface area of thin ice films at 77 K reported in this article is in excellent agreement with previous results (100-400 m^2/g) for thicker films [12,18-21].

2. *Ice films deposited at 196 K.*

In these experiments ice films were prepared similarly to those at 77 K. Deposition rates were varied from 1.9 to 6.4 mg/min and the flow tube was cooled to 196 K by submerging it in a dry ice/ methanol slush. After the deposition, the flow tube was cooled to 77 K for the BET measurement by imersing it in liquid nitrogen. The linearity and intercept in the BET plot imply that the adsorption isotherm is well behaved. After subtracting the surface area of the glass wall (determined in a blank experiment), wc obtain a value of 6.2 for the ratio of the ice surface area to the geometric area. The result suggests that ice films prepared in this manner arc not smooth, non-porous solids and the usc of the geometric area for the determination of the uptake coefficients or reaction probabilities in some previous studies is not valid.

A series of experiments were performed for ice mass ranging from 10.3 to 524.6 mg (thickness = 1.04 to 47.4 μm). The results arc listed in Table 1 and plotted in Figure 5, The deposition rate was varied from 1.9 to 6.4 mg/min. The ratio of the ice surface area to the geometric area was found to vary from 1.6 to 9.3. The specific surface area (S_g) was found to vary from 5.92 m^2/g for thinner ices to about 0.21 m^2/g for thicker ices; these values arc in good agreement with previous results (0.40 -10.8 m^2/g) obtained for thicker ice films in a separate apparatus [12].

As seen in Figure 6, S_g decreases markedly as the mass (or thickness) increases, especially below about SO mg. This is in contrast to the results for ices deposited at 77 K (see above). The average particle size, d, is inversely proportional to Sg: $d = 6/(\rho_t S_g)$, where ρ_t is the true density of the ice. The observed decrease in Sg suggests that the ice particle size increases as the film becomes thicker and the total area does not increase linearly with the mass. This increase in granule size with thickness has been observed previously by using ESEM to examine ice films forming near 200 K. [13]

HCl Uptake Measurements

The uptake of HCl in the ice films characterized above was measured at 196 K The total amount of HCl adsorbed was obtained by integrating the HCl flow rates and

calibrated HCl signal intensities over the observation time. The mass was varied from 11.3 to 496 mg (thickness =1.04 to 44.8 μm). The HCl partial pressure was held at about 5 x 10-7 Torr in a total pressure of 0.47 Torr. The average flow velocity was 625 cm/s. The results arc shown in Figure 8, which displays the HCl uptake as a function of mass. The average uptake was measured to be about 1.0 x 1014 molecules/cm^2 for thicker icc films (>100 mg). The amount of HCl adsorbed on borosilicate substrates (less than 1 x 10^{13} molecules/cm^2) was found to be much smaller than on icc films ; wc have corrected for this contribution.

In earlier work wc used a layer model to estimate the HCl surface density and obtained a value of 2 x 10^{13} molecules/cm^2 at 188 K and an HCl pressure of 2.1 x 10-7 Torr.[8] As noted in our previous study the HCl uptake is a complex function of temperature, HCl partial pressures, and ice film thickness. in addition, icc surface areas are very sensitive to the deposition temperature. Our previous investigation was performed at temperatures of 1 S8 K and 193K. The variation of 3-8 K may result significant difference in sur-face areas. Considering the simplicity of the model used, the sensitivity to experimental parameters, and the combined experimental errors, the HCl uptake reported here is in reasonably good agreement with the earlier estimate.

Acknowledgment. The research described in this article was performed at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration. We thank Tom A. Hardt of ElectroScan Co1 p. for his assistance in obtaining scanning electron micrographs. R. S.'1'. gratefully acknowledges the financial support from Maj and 'l'or Nessling Foundation.

References and Notes

(1) *Scientific Assessment of Ozone Depletion: 1994*; World Meterologica Organization Global Ozone Research and Monitoring Project, Report No. 37

(2 Leu, M-T. *Geophys. Res. Lett.* **988**, *15*, 7

(3) Chu, L. T.; Leu, M-T.; Keyser, L. F. *J. Phys. Chem.* **1993**, *97*, 7779.

(4) Molina, M. J.; Tso, T-L.; Molina, L. T.; Wang, F. C. Y. *Science* **1987**, *238*, 253

(5) Abbatt, J. P. D.; Beyser, K. D.; Fucaloro, A. F.; McMahon, J. R.; Wooldridge, P. J.; Zhang, R.; Molina, M. J. *J. Geophys. Res.* **1992**, *96*, 5819.

(6 Leu, M-T. *Geophys. Res. Lett.* **988**, *15*, 85

(7) Tolbert, M. A.; Rossi, M. J.; Golden, D. M. *Science* **1987**, *238*, 258

(8) Chu, T., Leu, M-T.; Keyser, L. F. *J. Phys. Chem.* **993**, *97*, 2798

(9) Hanson, D R.; Ravishankara, A. R. *J. Geophys. Res.* **991**, *96*, 58

o Keyser, L. F.; Moore, S. B.; Leu, M-T. *J. Phys. Chem.* ≥≥ , *95*, 5496.

(11) Keyser, L F., Leu, M-T.; Moore, S. B. *J. Phys. Chem.* **1993**, *97*, 2800.

(12) Keyser, L. F.; Leu, M-T. *J. Colloid Interface Sci.* **1993**, *155*, 137.

(13) Keyser, L. F.; Leu, M-T. *Microscopy Res. Tech.* **1993**, *25*, 434.

(14) Gregg, S. J.; Sing, K. S. W., "Adsorption, Surface Area and Porosity", Academy Press, New York, 1982.

(15) Fisher, B. B.; McMillan, W. G. *J. Phys. Chem.* **1958**, *62*, 494.

(16) Knowles, A. J.; Moffat, J. B. *J. Colloid Interface Sci.* **1971**, *37*, 860.

(17) McClellan, A. L.; Harnsberger, H. F. *J. Colloid Interface Sci.* **1967**, *23*, 577.

(8) Mayer, E.; Pletzer, R. *Nature*, **1986**, *319*, 298.

(9) Schmitt, B.; Ocampo, J.; Klinger, J. *J. dePhys.* **1≥87**, *48C1*, 58

(20) Ghormley, J. A. *J. Chem. Phys.* **1≥67**, *46*, 32

(2) Bar-Nun, A.; Dror, J.; Kochavi, E.; Laufer, D. *Phys. Rev. B.* **1987**, *35*, 2427.

'l'able 1. Summary of measurements of ice surface areas at 77 K and 196 K

T (K)	Mass (mg)	Rate (mg/min)	h[a] (μm)	A (m^2)	Sg(m^2/g)	Ratio[b]
77	19.7	2.0	1.78	6.9	350.2	305
	39.4	2.0	3.56	12.7	321.3	724
	63.9	1.6	5.78	17.4	273.1	928
	93.9	2.4	8.49	24.1	256.2	1300
	118.5	2.4	10.7	48.9	411.7	2778
	119.1	2.4	10.8	40.0	336.2	2269
				av =	324.8±56.1	
196	18.7	1.9	1.69	0.028	1.50	1.6
	41.2	1.9	3.73	0.021	0.51	1.2
	66.5	2.0	6.01	0.043	0,65	2.4
	92.4	2.1	8.35	0.051	0.55	2.9
	100.2	2.0	9.06	0.089	0.89	5.1
	103.0	2,1	9.31	0.113	1.10	6.4
	204.8	2.0	18.5	0.043	0.21	2.4
	211.0	2.1	19.1	0.064	0.30	3.6
	328.8	2.0	29.7	0.109	0.33	6.2
	379.2	2,5	34.3	0.084	0.22	4.8
	210.0	3.5	19.0	0.067	0.32	3.8
	10.3	6.4	1.04	0.061	5.92	3.5
	30.6	6.4	3.09	0.040	1.31	2.3
	33.1	6.4	3.35	0.066	1.99	3.8
	130.0	6.4	11.8	0.108	0.83	6.2
	132.0	6.4	11.9	0.073	0.55	4.2
	199.3	6.4	18.0	0.108	0.54	6.2
	260.4	6.4	23.5	0.142	0.55	8.1
	268.2	6.4	24,2	0.102	0.38	5.8
	360.5	6.4	32.6	0.163	0.45	9.3
	400.0	6.4	36.2	0.085	0.21	4.8
	443.1	6.4	44.8	0.129	0.29	7.3
	524.6	6.4	47,4	0.129	0.25	7.3

Notes:

a. Calculated from the sample mass, the geometric area and the bulk density (0.63 g/cm3) measured near 200 K (1 2).

b. Ratio of ice surface area/geometrical ea.

Figure Captions

Figure 1, Schematic diagram of the environmental scanning electron microscope used to examine the morphology of icc films.

Figure 2. Schematic diagram of the experimental apparatus used to measure ice surface areas.

Figure 3. Electron micrographs of an H_2O ice film formed by vapor deposition onto a borosilicate substrate.

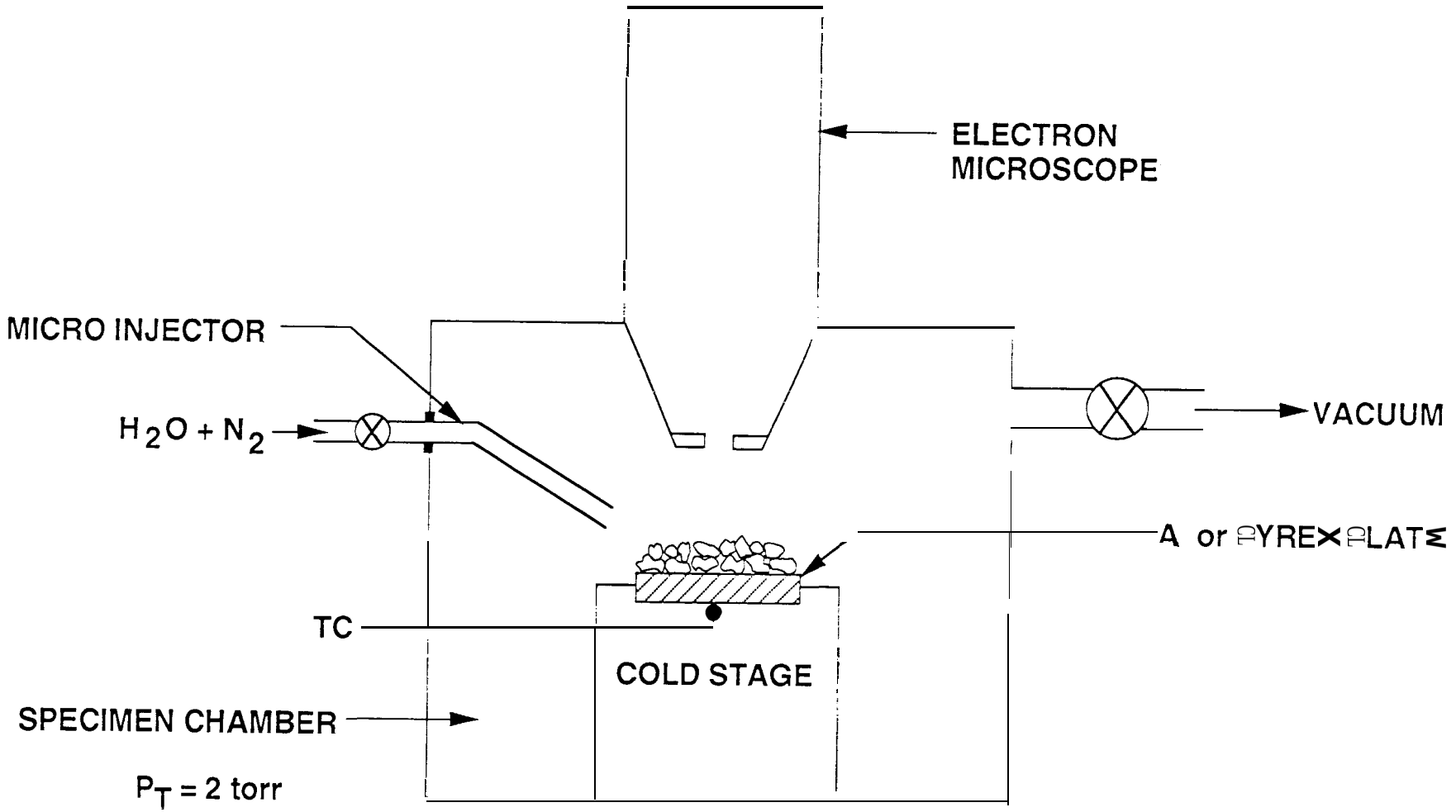
Figure 4. Typical data of the BET adsorption isotherm for icc film formed by vapor deposition at 77 K.

Figure 5. Total ice surface areas vs. mass (thickness) for films deposited at 196 K.

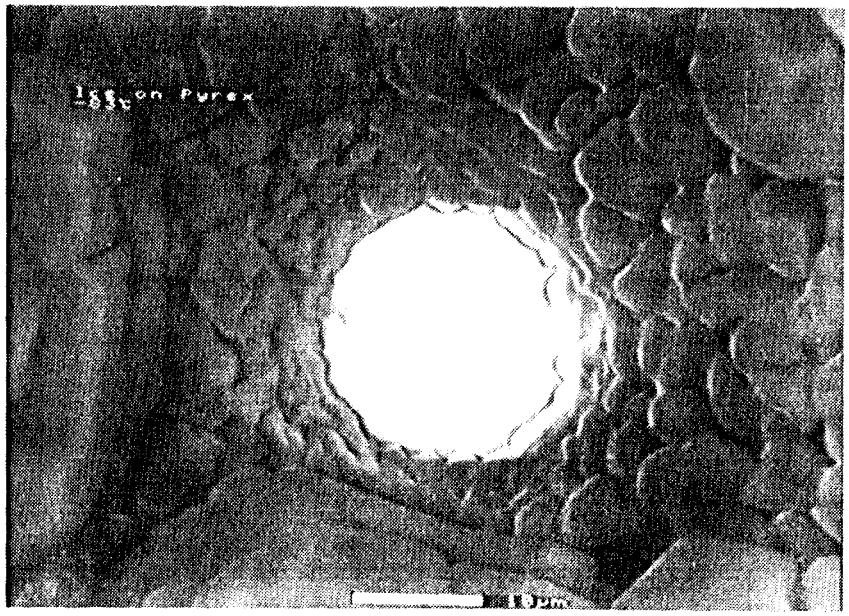
Figure 6. Specific surface areas vs. mass (thickness) for films deposited at 196 K.

Figure 7. Summary of HCl uptake measurements for ice films formed by vapor deposition at 196 K.

SCANNING ELECTRON MICROSCOPY OF ICE FILMS



TOP VIEW



SIDE VIEW

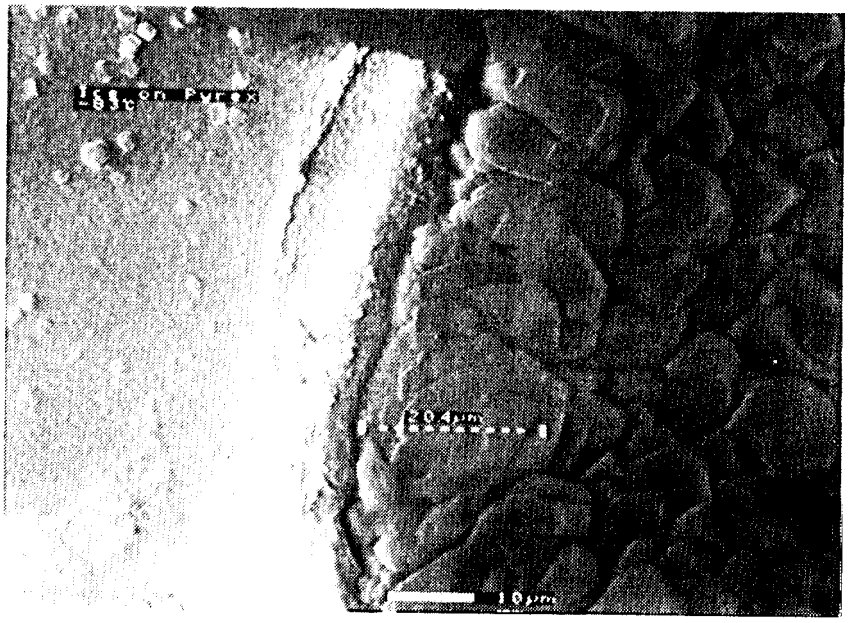


Fig. 2

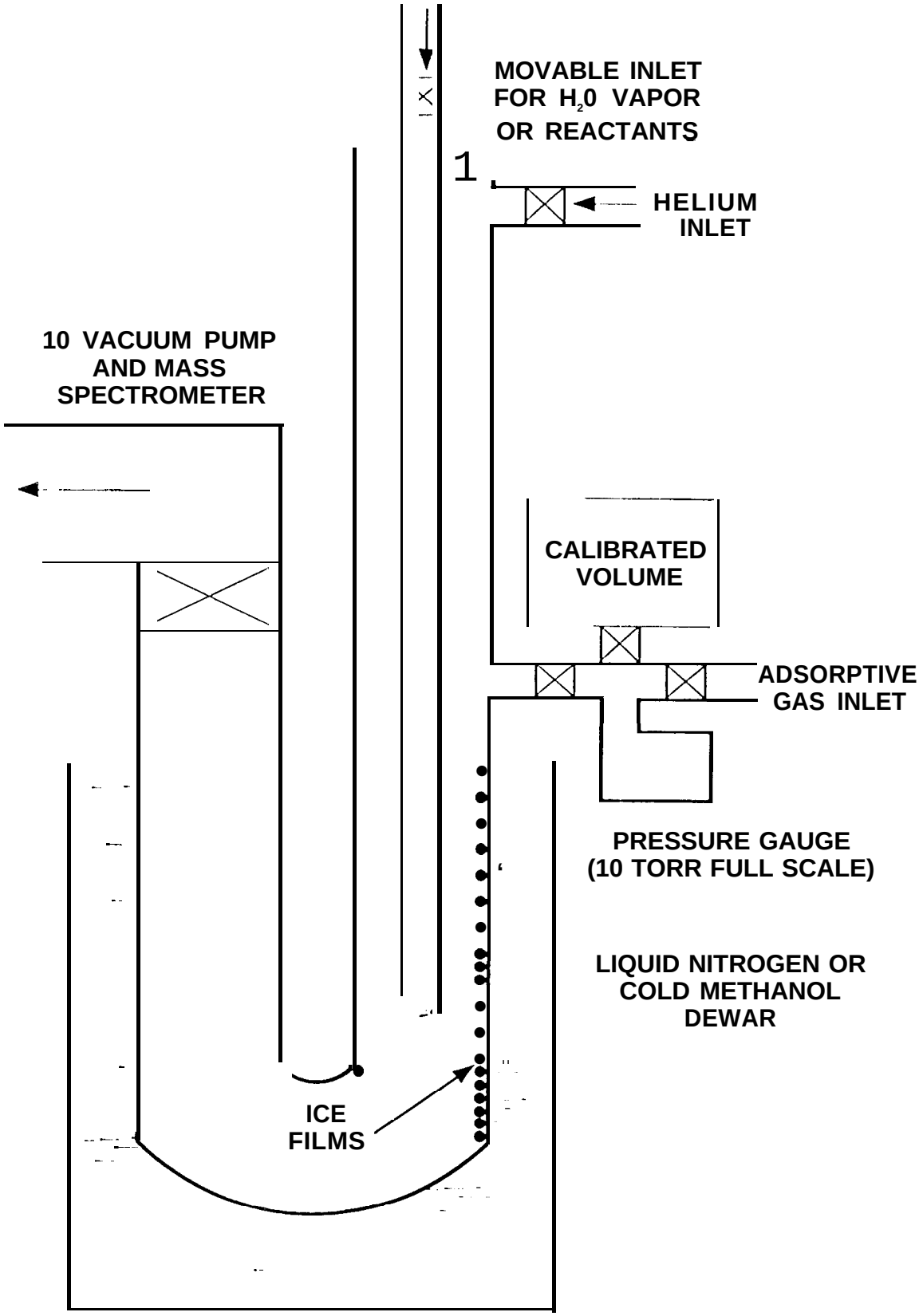

MOVABLE INLET
FOR H_2O VAPOR
OR REACTANTS
1
HELIUM
INLET
10 VACUUM PUMP
AND MASS
SPECTROMETER
CALIBRATED
VOLUME
ADSORPTIVE
GAS INLET
PRESSURE GAUGE
(10 TORR FULL SCALE)
LIQUID NITROGEN OR
COLD METHANOL
DEWAR
ICE
FILMS

Fig. 3

Kr Adsorption on Ice Formed at 77 K

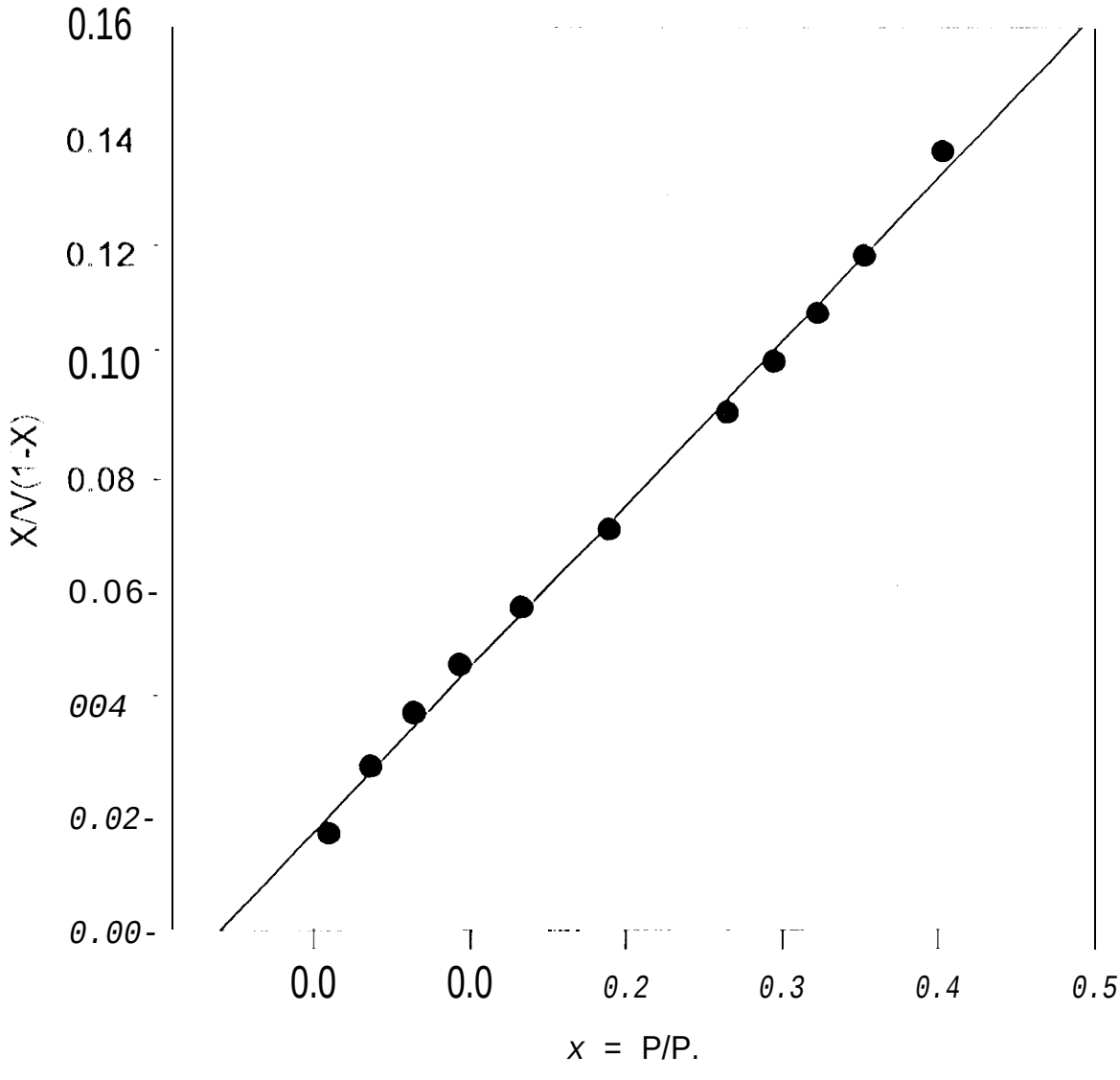


Fig. 4

Ice Surface Area

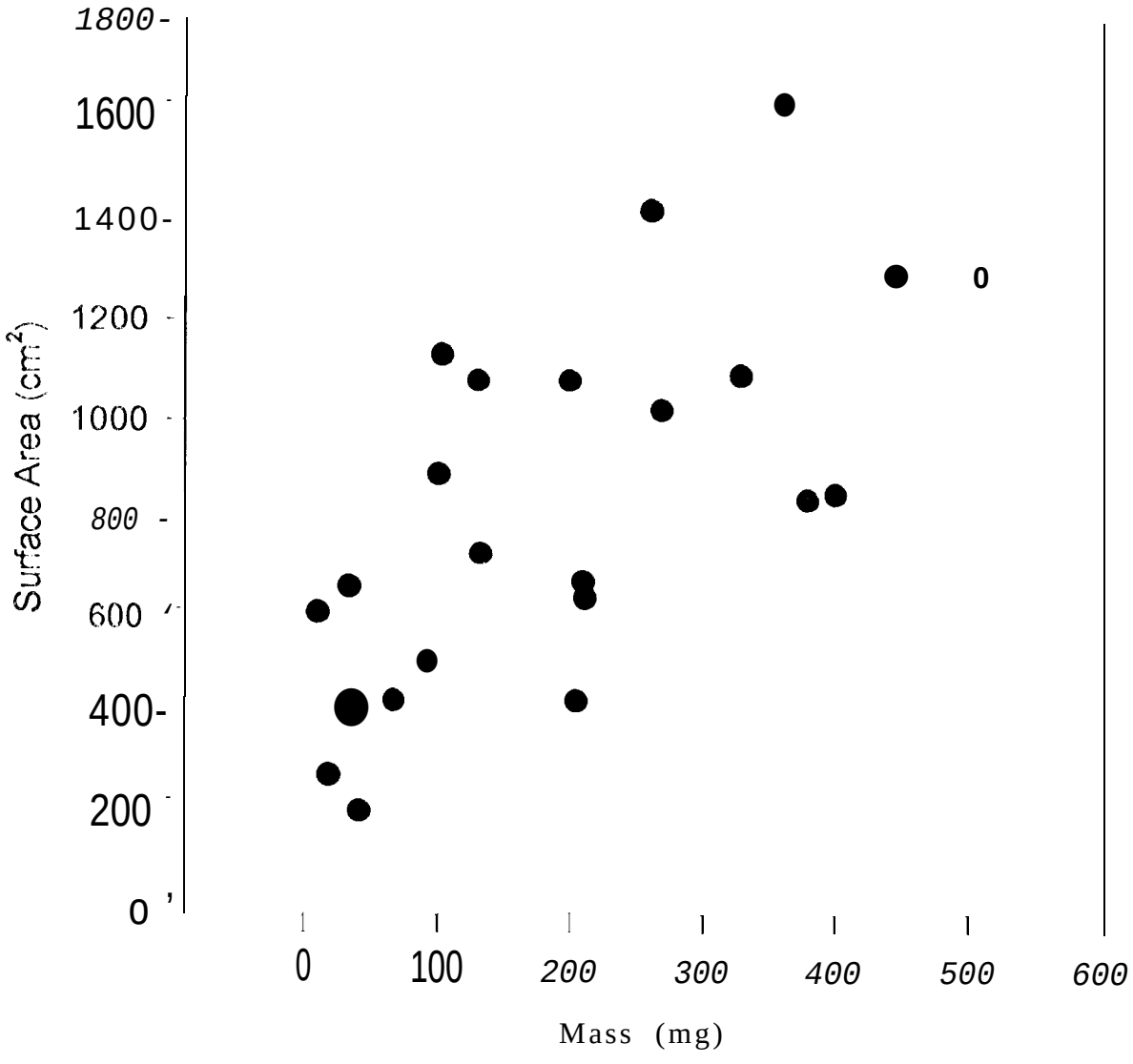


Fig. 5

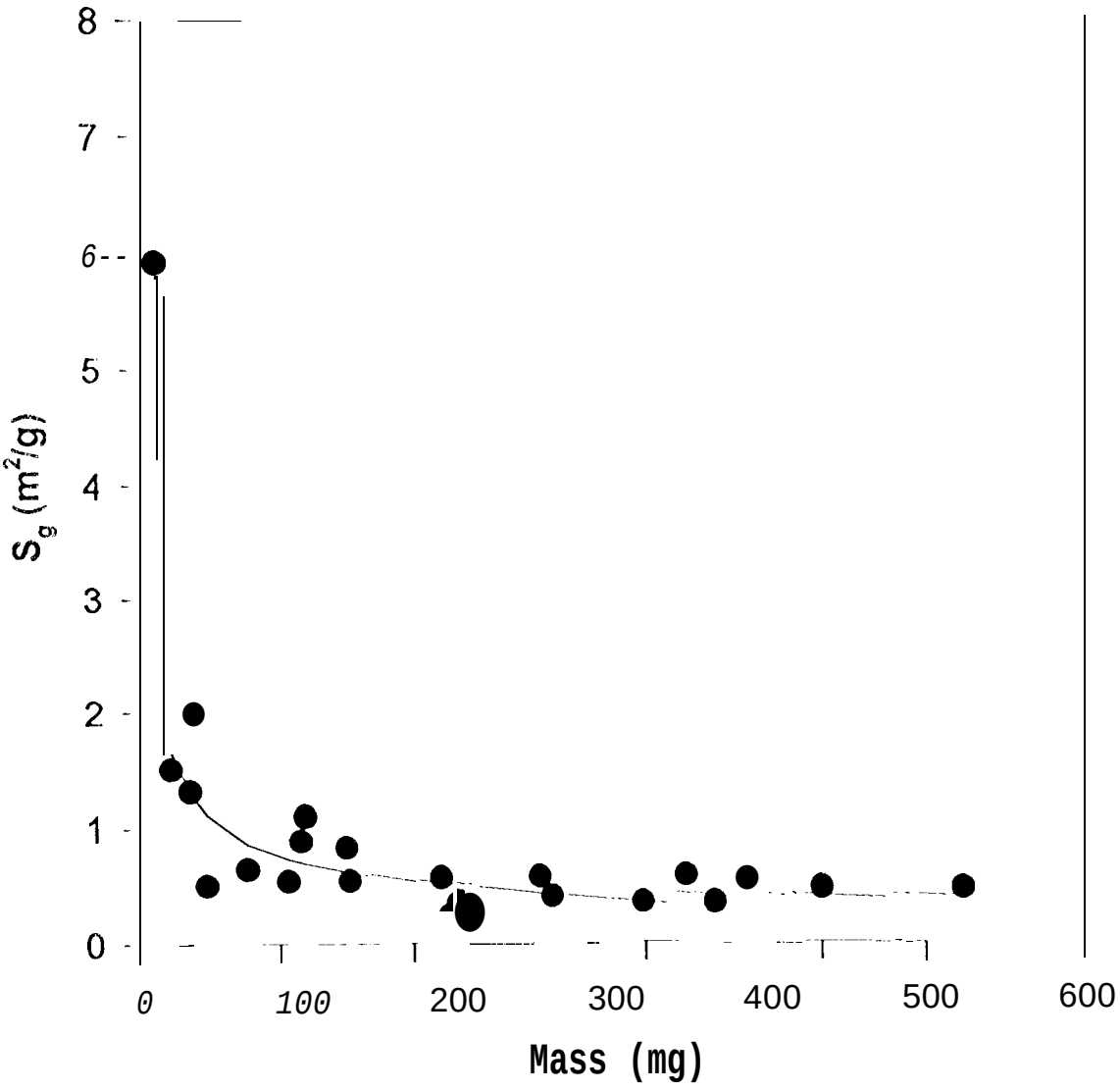

Ice Deposited at 196 K
8
7
6
5
4
3
2
1
0
S_g (m^2/g)
0
100
200
300
400
500
600
Mass (mg)

Fig. 6

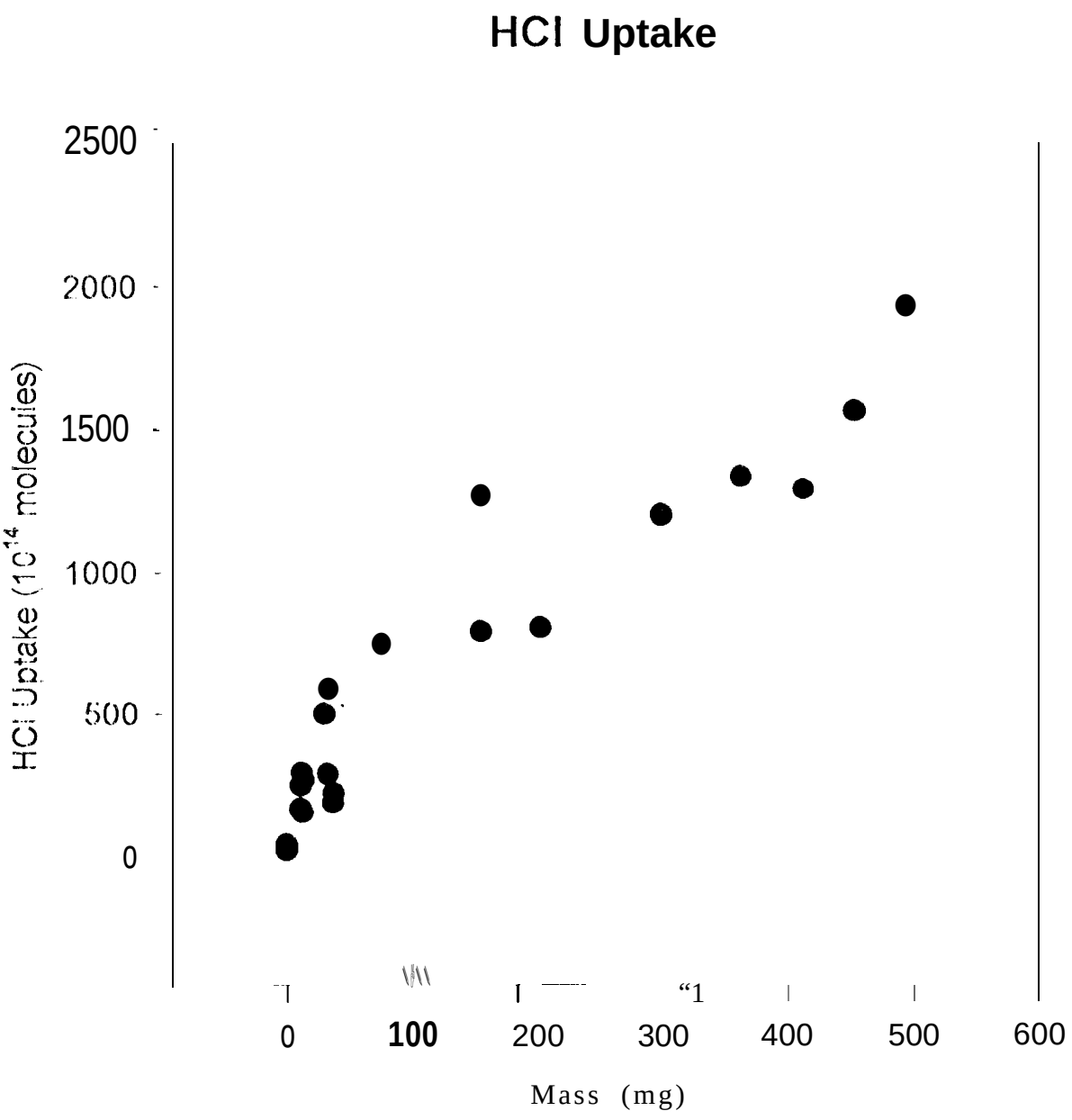

HCl Uptake
2500
2000
1500
1000
500
0
HCl Uptake (10^{14} molecules)
0
100
200
300
400
500
600
Mass (mg)

Fig. 7