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## ENERGY & ENVIRONMENT DIVISION

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SOOT PARTICLES

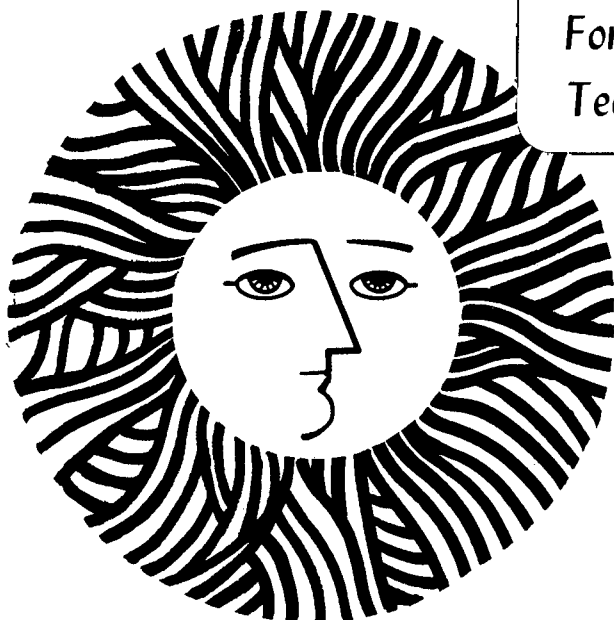
W.H. Benner, R. Brodzinsky, and T. Novakov

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OXIDATION OF SO<sub>2</sub> IN DROPLETS WHICH CONTAIN SOOT PARTICLES\*W. H. Benner, R. Brodzinsky,<sup>†</sup> and T. NovakovLawrence Berkeley Laboratory  
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A laboratory fog chamber was constructed in which water droplets or droplets containing soot particles could be exposed to SO<sub>2</sub>. For wet particles exposed to 0.007 ppm < [SO<sub>2</sub>] < 222 ppm, the maximum experimentally observed carbon-normalized rate of particulate sulfate formation was  $d[\text{SO}_4^{2-}/\text{C}]/dt = 8 \times 10^{-6} \text{ g} \cdot \text{SO}_4^{2-}/\text{g} \cdot \text{C} \cdot \text{sec}$ . The rate expression,

$$\frac{-d[\text{S(IV)}]}{dt} = k[\text{C}] \cdot \frac{\alpha[\text{S(IV)}]^2}{1 + \beta[\text{S(IV)}] + \alpha[\text{S(IV)}]^2},$$

was determined for the reaction. Under atmospheric conditions, this rate expression indicates that the effective order for the oxidation of S(IV) depends on environmental conditions and ranges between 0.1 and 1.6.

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## INTRODUCTION

The chemical reactions used to describe sulfate formation in the atmosphere are numerous; Middleton et al. (1980) recently compared the importance of several of these pathways.  $\text{SO}_2$  oxidation reactions which involve liquid water have received attention in the literature. Penkett et al. (1979) reported that the oxidation of  $\text{SO}_2$  by dissolved  $\text{O}_3$  and  $\text{H}_2\text{O}_2$  can lead to sulfate formation in clouds. Wolff et al. (1979) presented ambient sampling data which suggested that particulate sulfate was formed by two mechanisms: one involved photochemical oxidation; the other proceeded by an  $\text{O}_3$ -fog droplet route. Enger and Högström (1979) found that the rate of  $\text{SO}_2$  oxidation in a power plant plume increased when the plume relative humidity (RH) was high, and similarly, Dittenhoefer and dePena (1978) reported that after a relatively dry power plant plume merged with a nearly water-saturated cooling tower plume, sulfate formed on the power plant plume particles. Johnstone and Mall (1960), using a laboratory fog chamber, found that  $\text{SO}_2$  was oxidized rapidly by solution droplets which contained  $\text{Mn}^{2+}$ , and Penkett and Garland (1974) observed sulfate formation in droplets exposed to  $\text{SO}_2$  and  $\text{O}_3$ . Although the experiments were not conducted in the dispersed phase, Penkett, Jones, and Eggleton (1979) collected rainwater and assayed its potential to oxidize  $\text{SO}_2$ . Novakov et al. (1974) observed that sulfate formed when soot particles were exposed to  $\text{SO}_2$  and that the soot-catalyzed reaction was enhanced at increased relative humidity. In other studies in our laboratory, Brodzinsky et al. (1980) showed that sulfite was oxidized to sulfate by aqueous suspensions of activated carbon, acetylene soot, and natural gas soot. Their flask-type reactions showed that the rate of oxidation was independent of pH when  $\text{pH} < 7.6$ .

Even though modelling studies have shown that the soot oxidation of  $\text{SO}_2$  is an important pathway for the formation of ambient sulfate (Middleton et al., 1980; Chang et al., 1981) and that the requisite soot particles have been found

in all rural and urban sampling sites (Rosen et al., 1980; Rosen and Bodhaine, 1981), this reaction has not been clearly observed in the atmosphere because competing reactions are not easily isolated. Also definitive experiments have not been reported that show that the soot mechanism can proceed in dispersed droplets. To answer these questions, we constructed a laboratory fog chamber in which stable fogs could be exposed to  $\text{SO}_2$ , and thereby reactions that could occur in clouds, fogs, and plumes could be studied. Additional flask-type reaction studies were also conducted to elucidate the soot-fog- $\text{SO}_2$  pathway. The fog chamber results presented in this paper are not intended to be a rigorous kinetic study, but the study was conducted to show that  $\text{SO}_2$  can be oxidized in droplets which contain soot particles. However, the combination of the fog chamber results with the kinetic equation determined from the flask-type reaction study supplies a body of information that can be introduced into computer models so that the relative importance of the soot-fog- $\text{SO}_2$  mechanism for sulfate formation in the atmosphere can be evaluated.

#### EXPERIMENTAL

Figure 1 shows a diagram of the laboratory fog chamber and associated equipment. Carbon particles were introduced into an air stream by nebulizing an aqueous suspension of commercially available activated carbon (Nuchar-SN, Wesvaco). Nuchar was used as a model system since large quantities of urban soot are difficult to obtain, and Nuchar behaves like acetylene and natural gas soots (Brodzinsky, 1981). The Nuchar was extracted with several washings in deionized water and, when used, had an elemental composition as shown in Table I. The air stream of suspended soot particles was humidified by passage over heated water. Then the flow stream was cooled to cause liquid water to condense onto the nebulized particles, and the resulting stream of fog droplets was introduced into the bottom of a fog chamber (0.35 m square x 2.7 m

tall) and  $\text{SO}_2$  was added. The fog droplets were forced upwards through the chamber at a velocity which permitted approximately a 30-min reaction time between the droplets and  $\text{SO}_2$ . A prefired quartz (800°C for 12 hr) and a Fluoropore (unlaminated, 0.5- $\mu\text{m}$  pore, Millipore Corp.) filter were used to collect samples simultaneously. Sampling time was 2 hours. Critical orifices controlled the flow through each filter, and care was taken to keep filter loading low enough so that the pressure drop across the critical orifices did not change during collection (Urone and Ross, 1979). Two optional techniques were used to dry the droplets so that reactions involving liquid water did not occur on the filters. The first is shown in Fig. 1, in which the filter holders and tubing leading to the filter holders were heated to decrease the relative humidity of the air stream to at least 30%. The temperature of the air stream (50°C) was monitored to guarantee proper heating. In the second drying technique, the heated filter manifold was replaced with two diffusion driers connected in series. Each drier was a 7.5-cm diameter x 42-cm long plexi-glass drying tube, filled with silica gel, and fitted concentrically with a 2-cm diameter x 42-cm long tubular screen through which the droplets were drawn. The diffusion driers dried the droplets and decreased the RH of the air stream to  $\sim 10\%$ . The driers removed  $\sim 90\%$  of the  $\text{SO}_2$  when the chamber  $[\text{SO}_2] = 180$  ppm and greater than 95% of the  $\text{SO}_2$  when chamber  $[\text{SO}_2] < 10$  ppm.

After collection of particles, the Fluoropore filters were extracted by vigorously shaking them for 1 hour in several mL of deionized water, after which the extract was filtered through a 0.22- $\mu\text{m}$  pore Millipore filter (low extractable type; pre-extracted twice in deionized water). The extract was analyzed by ion chromatography (System 14, Dionex Corp.). A 0.002 M NaOH + 0.0035 M  $\text{Na}_2\text{CO}_3$  eluent was used in the ion chromatographic analysis so that an occasionally observed phosphate contaminate peak eluted after the sulfate peak

and thereby did not interfere with earlier eluting peaks. The quartz filters were analyzed for total carbon by combusting the collected carbon to  $\text{CO}_2$  and then determining the  $\text{CO}_2$  coulometrically ( $\text{CO}_2$  Coulometer, Coulometrics, Inc.). Potential interferences in the  $\text{CO}_2$  determination were selectively scrubbed according to manufacturer's guidelines: evolved  $\text{SO}_2$  was adsorbed on  $\text{BaCrO}_4$ , halogens adsorbed on Ag metal, and  $\text{NO}_x$  was oxidized to  $\text{NO}_2$  and adsorbed on  $\text{MnO}_2$ .

The flask-type reactions with aqueous suspensions of soot were described earlier (Brodzinsky et al., 1980) and the procedures are summarized here.  $\text{H}_2\text{SO}_3$  (diluted final concentration between  $7 \times 10^{-8}$  M and  $1 \times 10^{-3}$  M) was added to a flask containing several hundred milliliters of a constantly stirred aqueous suspension of Nuchar in which the particle concentration was between 0.002 and 0.32% w/v carbon. For  $\text{H}_2\text{SO}_3$  concentrations less than  $10^{-4}$  M, sulfite and sulfate were determined by ion chromatography. Above  $10^{-4}$  M  $\text{H}_2\text{SO}_3$ , sulfite concentrations were determined by iodometric titrations while sulfate was measured turbidimetrically only in selected runs. The pH of a soot suspension was controlled by the buffering capacity of the  $\text{SO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{HSO}_3^-$ ,  $\text{SO}_3^{2-}$  system.

## RESULTS AND DISCUSSION

In order to see the effect of Nuchar, fog chamber runs were conducted in which the fog was produced by the nebulization of either a suspension of Nuchar or deionized water. The droplets were dried in these runs with the heated filter manifold. For all runs, the droplet residence time in the chamber was approximately 30 min. When deionized water droplets were exposed to  $\text{SO}_2$ , a limited amount of sulfate was detected (Fig. 2) in the filter samples. For water droplets exposed to  $\text{SO}_2$  (.007-222 ppm), the calculated solution equilibrium pH falls between 5.0 and 2.8. In this pH range, the S(IV) species are almost entirely in the form of  $\text{HSO}_3^-$  and  $\text{SO}_2 \cdot \text{H}_2\text{O}$  (cf. Fig. 1 in Carmichael and Peters, 1979). Since only  $\text{SO}_3^{2-}$  has been reported to undergo air ( $\text{O}_2$ )



oxidation in aqueous solution (Penkett and Garland, 1979; Scott and Hobbs, 1967; Beilke, Lamb, and Müller, 1975), limited formation of  $\text{SO}_4^{2-}$  in the fog droplets by  $\text{O}_2$  oxidation is expected because of the relatively low  $[\text{SO}_3^{2-}]$ . The data for sulfate formation in deionized water droplets contain much scatter and are presented here only to show the difference in sulfate formation between these droplets and droplets which contain Nuchar particles.

When a suspension of Nuchar particles is nebulized and the resulting droplets are exposed to  $\text{SO}_2$ , the rate of sulfate formation was found to be significantly faster than the rate observed for deionized water droplets exposed to  $\text{SO}_2$ . A comparison of the two sets of data in Fig. 2 shows the increased  $\text{SO}_4^{2-}$  formation rate observed for wet Nuchar particles and shows that the wet Nuchar particles exposed to 0.007 ppm  $\text{SO}_2$  produced more  $\text{SO}_4^{2-}$  than deionized water droplets exposed to 222 ppm  $\text{SO}_2$ . The importance of Nuchar in  $\text{SO}_4^{2-}$  formation is further substantiated by the fact that normalization of the  $\mu\text{g SO}_4^{2-}/\text{m}^3 \cdot \text{sec}$  values for wet Nuchar particles in Fig. 2 to the Nuchar concentration ( $\mu\text{g C}/\text{m}^3$ ) significantly reduced the scatter in the data. The normalized data are plotted in curve 2 in Fig. 3. The normalization reduces the scatter because a large run-to-run variation in the Nuchar concentration occurred.

In Fig. 3 the carbon-normalized rate of sulfate formation for Nuchar droplets exposed to  $\text{SO}_2$  is plotted for three separate sampling techniques. The data for curve 1 were obtained from fog chamber runs in which the droplets were dried with a diffusion drier before filtration. The data for curve 2 were obtained from fog chamber runs in which the heated filter manifold was used to dry the droplets before filtration. Curve 3 data were obtained as follows: The heated filter manifold was separated from the top of the fog chamber and the nebulizer was connected directly to the inlet of the heated manifold. A quartz and a Fluoropore filter were loaded simultaneously with an

amount of Nuchar that was similar to the amount of Nuchar collected during a typical fog chamber run. After collection,  $\text{SO}_2$  in dry air (dew point =  $-30^\circ\text{C}$ ) was drawn through the loaded filters for 2 hours (2 hours was the sampling time for a fog chamber run) while the air through the filter was maintained at  $50^\circ\text{C}$ . To calculate the carbon-normalized rate of sulfate formation, the carbon loading on the quartz filter was used along with the sulfate loading on the Fluoropore filter.

A comparison of the three curves in Fig. 3 indicates that sampling techniques must be carefully chosen. The data in curve 2 overestimates the rate of sulfate formation because the heated filter manifold did not properly quench the reaction. The heating prevented reactions involving liquid water from occurring on the filter but did not prevent  $\text{SO}_2$  oxidation via a "high" temperature mechanism that occurred on hot/dry Nuchar as shown by the curve 3 data. An approximate correction of the curve 2 data (droplets dried by heating) would be to subtract the effect of the curve 3 data ( $\text{SO}_2$  through a heated filter). Such a correction is only approximate because the artifact determination experiments were not identical to fog chamber runs. In the artifact determination experiments,  $\text{SO}_2$  was drawn through a loaded filter, while in a fog chamber run the filter was being loaded as  $\text{SO}_2$  was drawn through it; and therefore in the fog chamber runs not all the sampled Nuchar was exposed to  $\text{SO}_2$  for 2 hours. The artifact determination experiments are thought to represent an upper limit for artifact formation in the heated filter runs and are included to point out the problems that can occur when heating is used to quench a reaction between a wet Nuchar particle and  $\text{SO}_2$ .

Figure 4 contains a family of curves describing the oxidation of S(IV) on wet Nuchar particles having various initial  $\text{H}^+$  concentrations. The family of curves was calculated from a reaction rate expression obtained from a flask-type

reaction study in which aqueous soot suspensions were exposed to a large range of initial S(IV) concentrations (Brodzinsky, 1981). The flask-type reaction study indicated that regardless of the initial [S(IV)] or soot concentration  $[C_x]$ , all the S(IV) was eventually oxidized to  $SO_4^{2-}$ , and the following oxidation mechanism was developed from the data:

$$\frac{d[S(IV)]}{dt} = k[C_x] \cdot \frac{\alpha[S(IV)]^2}{1 + \beta[S(IV)] + \alpha[S(IV)]^2} \quad (\text{Eq. 1})$$

where  $[C_x]$  = Nuchar concentration in droplet, (g/L)

$$[S(IV)] = [SO_2 \cdot H_2O] + [HSO_3^-] + [SO_3^{2-}]$$

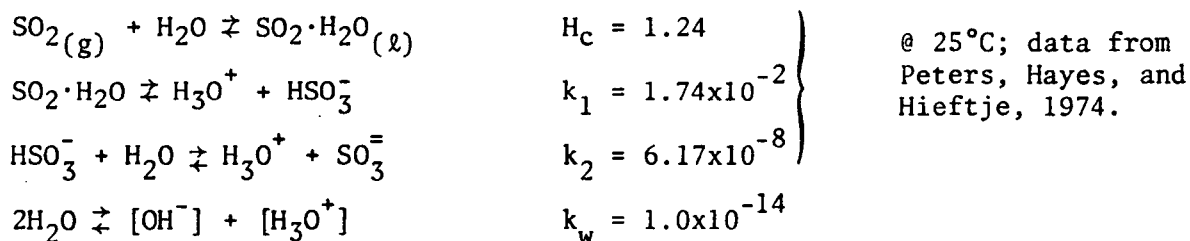
$$\alpha = 4.915 \times 10^8 \text{ L}^2/\text{mole}^2$$

$$\beta = 2.956 \times 10^5 \text{ L/mole}$$

$$k = 1.036 \times 10^{-7} \text{ mole/g} \cdot \text{sec}$$

Equation 1 describes an oxidation mechanism which is not sensitive to solution pH for  $\text{pH} < 7.6$  (Brodzinsky et al., 1980). The family of curves in Fig. 4 indicates a pH effect, but pH only becomes a factor when soot suspensions are exposed to  $SO_2$ . The pH effect is related to the absorption of  $SO_2$  by the droplet. For example, two droplets, one of which has an initial pH of 3 and the other a pH of 5, are equilibrated with 1 ppm  $SO_2$ . The droplet with the lower initial pH will have a lower equilibrium [S(IV)] after each is equilibrated with 1 ppm  $SO_2$ . The oxidation rate will be similarly slower in the pH = 3 droplet, not because of an  $H^+$  effect but because of the relatively lower [S(IV)]. The family of curves was calculated\* assuming that the droplet

\*Calculations were made assuming the following equilibria:



was buffered at a specified pH and was then equilibrated with  $\text{SO}_2$  to produce a certain equilibrium  $[\text{S(IV)}]$  before  $\text{S(IV)}$  oxidation started. The resultant  $[\text{S(IV)}]$  was then used to calculate the reaction rate using Eq. 1.

The dashed line in Fig. 4 shows the  $\text{S(IV)}$  oxidation rate expected for wet Nuchar particles in equilibrium with  $\text{SO}_2$  and 320 ppm  $\text{CO}_2$ . This curve was calculated assuming that the Nuchar droplet initially had a pH of 7 (not buffered) and was then equilibrated with  $\text{SO}_2$  and 320 ppm  $\text{CO}_2$  to produce a certain equilibrium  $[\text{S(IV)}]$  and equilibrium pH before  $\text{S(IV)}$  oxidation started. The resulting  $[\text{S(IV)}]$  was used to calculate the reaction rate using Eq. 1. It was also assumed that the Nuchar possessed no pH-altering species. Figure 4 also contains a plot of the fog chamber data (curve 1, Fig. 3) for comparison.

The difference between the fog chamber data and the dashed line in Fig. 4 is due to the alkaline nature of Nuchar. The release of alkaline species into the droplet from the Nuchar neutralized some of the absorbed  $\text{SO}_2 \cdot \text{H}_2\text{O}$  and/or  $\text{HSO}_3^-$  and thus the equilibrium  $[\text{S(IV)}]$  was larger than that predicted by Henry's Law for pure water that was equilibrated with  $\text{SO}_2$  and 320 ppm  $\text{CO}_2$ . This neutralization increased the oxidation rate because it brought more  $\text{S(IV)}$  into the droplet. The magnitude of the difference between the fog chamber data line and the dashed line depends on the  $[\text{SO}_2]$ . At low  $[\text{SO}_2]$ , the alkaline species on the soot particles attract into solution more  $\text{S(IV)}$  than would be expected for pure water exposed to  $\text{SO}_2$ , and thus these alkaline species strongly influence the resultant  $[\text{S(IV)}]$ . At high  $[\text{SO}_2]$ , the dissolved  $\text{SO}_2$  overwhelms the buffering capacity of the alkaline species and the  $[\text{SO}_2]$  becomes the dominant factor for controlling the resultant  $[\text{S(IV)}]$ . Therefore, at high  $[\text{SO}_2]$  the fog chamber data and the dashed line converge in Fig. 4. The maximum experimentally observed  $\text{SO}_4^{2-}$  formation rate is  $8 \times 10^{-6}$  g  $\text{SO}_4^{2-}$ /g C-sec and the maximum rate calculated from Eq. 1 is  $1.3 \times 10^{-5}$  g  $\text{SO}_4^{2-}$ /g C-sec.

An attempt was made to determine the nature of the alkaline species on the Nuchar. Titration of an aqueous Nuchar suspension with acid showed that the species were a myriad of weak bases, each present in relatively small amounts. Because the titration curve of pH vs. ml of acid added was almost a straight line (Fig. 5), dissociation constants for the weak bases could not be determined and thus it is impossible to mathematically model the pH characteristics of the aqueous Nuchar plus dissolved SO<sub>2</sub> system. The aberration in the titration curve at pH ≈ 6.3 was reproducible.

Experimentally, we determined the effect of weak bases on SO<sub>2</sub> absorption by soot suspensions. A weighed quantity of Nuchar was degassed at 10<sup>-3</sup> torr and 150°C overnight and then brought to atmospheric pressure under N<sub>2</sub>. Under a N<sub>2</sub> atmosphere, deoxygenated water was added to the degassed Nuchar and 1 ppm SO<sub>2</sub> in N<sub>2</sub> was bubbled (2 lpm) through the suspension (0.2 g C/200 ml) until equilibrium was attained (~ 20 hr). Under these oxygen-deficient conditions, the oxidation of S(IV) by wet Nuchar is repressed so that an equilibrium pH can be determined without severe interference from the H<sup>+</sup> that forms concurrently with SO<sub>4</sub><sup>2-</sup> formation. The results of duplicate bubbling experiments are presented in Table II.

For pure water equilibrated with 1 ppm SO<sub>2</sub> (25°C), the calculated [S(IV)]<sub>equil</sub> = 1.4 x 10<sup>-4</sup> M and pH<sub>equil</sub> = 3.8. For water buffered at pH = 4.0 and equilibrated with 1 ppm SO<sub>2</sub> (25°C), the calculated [S(IV)]<sub>equil</sub> = 2.2 x 10<sup>-4</sup> M. Experimentally (Table II) a suspension of 1 g C/l was equilibrated at 25°C with 1 ppm SO<sub>2</sub> in N<sub>2</sub> and at equilibrium: pH = 4.0, [S(IV)] = 2 x 10<sup>-4</sup> M, and [SO<sub>4</sub><sup>2-</sup>] = 5 x 10<sup>-5</sup> M. For this experimental run, 80% of the theoretical [S(IV)] for pH = 4.0 was obtained. The presence of the soot increased the [S(IV)] 0.6 x 10<sup>-4</sup> M over that expected for pure water equilibrated with 1 ppm SO<sub>2</sub>.

The buffering capacity of the weak bases maintained a higher than expected pH (4.0 vs. 3.8), even though  $1 \times 10^{-4}$  M of  $H^+$  was concurrently introduced into the suspension because of  $H_2SO_4$  formation. The weak bases exert an important effect on S(IV) oxidation by wet Nuchar particles because the weak bases draw additional S(IV) into solution, which in turn increases the oxidation rate. We have examined the acid/base properties of several other commercially available activated carbons, and these properties vary between types. We do not know at this time the acid/base nature of freshly generated atmospheric soot properties.

The soot particles in the ambient atmosphere come from a variety of mobile and stationary sources. Since it has been shown that diesel and natural gas soots behave similarly to Nuchar in terms of S(IV) oxidation (Brodzinsky, 1981), it is reasonable to extrapolate the Nuchar findings to the ambient atmosphere. From the rate expression (Eq. 1), the following equations can be developed:

$$-\frac{d[S(IV)]}{dt} = k[C_x] \cdot \frac{\alpha[S(IV)]^2}{1 + \beta[S(IV)] + \alpha[S(IV)]^2} = k' [f(SO_2, pH)]^n, \quad (\text{Eq. 2})$$

in which  $k' \equiv$  a constant,  $f(SO_2, pH) \equiv [S(IV)]$  as a function of  $SO_2$  and pH, and  $n \equiv$  effective reaction order for  $SO_2$ . Finally,  $n$  as a function of pH for a given  $[SO_2]$  can be plotted as shown in Fig. 6. The effective order for the oxidation of  $SO_2$  by wet Nuchar particles ranges between 0 and 2 depending on  $[SO_2]$  and pH. When droplets are exposed to  $SO_2$  and 320 ppm  $CO_2$ , a certain pH results. The line of pH due to  $SO_2$  and 320 ppm  $CO_2$  equilibria is shown in Fig. 6 and forms a boundary for region 3. In the atmosphere, rain water and atmospheric droplets have a pH = 5.6 when in equilibrium with 320 ppm  $CO_2$  in clean air and do not usually have a pH less than about 3 when collected from polluted air (Likens, 1979). If  $[SO_2] = 0.5$  ppm is taken as an upper limit

for the concentration of  $\text{SO}_2$  in the atmosphere (outside a plume), then region 1 in Fig. 6 shows that the effective order for  $\text{SO}_2$  oxidation by wet soot particles in the atmosphere falls between 0.9 and 1.6 for droplet pH between 3 and 5.6. In a plume the situation can be much different. At the higher  $[\text{SO}_2]$  commonly encountered in plumes, the effective order may be as low as 0.1 (region 3 in Fig. 6). If  $\text{NH}_3$  or other alkaline species are present in the droplets, the pH will be higher initially, i.e., before  $\text{SO}_4^{2-}$  formation, and the effective order for the atmospheric example could be considerably smaller than 0.9 (region 2 in Fig. 6). The effect of alkaline species on S(IV) oxidation will be smaller in the plume situation because the relatively high  $[\text{SO}_2]$  will produce a relatively low pH droplet. The concentrations of  $\text{NH}_3$  normally encountered in the atmosphere will not be adequate to change the pH of the plume droplet. Again it must be emphasized that pH affects S(IV) oxidation only because it determines  $[\text{S(IV)}]$ .

The effective order for S(IV) oxidation by wet soot particles (Fig. 5) will be useful to modellers of  $\text{SO}_2$  oxidation. In the past, models used to explain  $\text{SO}_2$  or S(IV) oxidation frequently employed reaction kinetics that were first order with respect to S(IV). Our findings indicate that it is more appropriate to employ a reaction order that changes with environmental conditions.

#### SUMMARY AND CONCLUSIONS

A laboratory fog chamber was constructed in which dispersed droplets, several micrometers in diameter, could be exposed to pollutant gases. In two separate sets of fog chamber tests, either water droplets which contained Nuchar particles or pure water droplets were exposed to  $\text{SO}_2$  (0.007 ppm to 222 ppm). The wet Nuchar particles oxidized  $\text{SO}_2$  to sulfate faster than the water droplets for all  $\text{SO}_2$  concentrations employed. For wet Nuchar particles, the maximum experimentally observed  $d[\text{SO}_4^{2-}/\text{C}]/dt = 8 \times 10^{-6} \text{ g SO}_4^{2-}/\text{g C-sec.}$

A generalized kinetic mechanism was combined with  $\text{SO}_2$  equilibria considerations so that the rate of  $\text{SO}_2$  oxidation by wet Nuchar particles could be determined for various  $\text{SO}_2$  exposures. For an extrapolation of the Nuchar data to wet soot particles exposed to  $\text{SO}_2$  in the atmosphere, the effective reaction order (n), in  $d[\text{SO}_4^{2-}/C]/dt = k[\text{SO}_2]^n$ , falls between 0.9 and 1.6 for atmospheric levels of  $\text{SO}_2$ . If  $\text{NH}_3$  is initially present in the atmospheric example, the effective order may be considerably smaller. At  $\text{SO}_2$  concentrations encountered in power plant plumes, the effective order of  $[\text{SO}_2]$  oxidation by wet soot particles could be as small as 0.1.

#### ACKNOWLEDGEMENT

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Table I. Composition of Nuchar-SN by weight percent.

Element	Percent
C	77.7
O	20.4
H	1.56
N	0.23
Fe	0.0110
Cr	0.0011
Ti	0.0011
Mn	0.0012

Table II. Results of bubbling 1 ppm SO<sub>2</sub> in N<sub>2</sub> through a deoxygenated Nuchar suspension.<sup>a</sup>

	pH <sub>equilibrium</sub>	[S(IV)] <sub>equilibrium</sub>	[SO <sub>4</sub> <sup>=</sup> ]
Soot suspension (prepared in pH <sub>0</sub> = 7 water), then equilibrated with SO <sub>2</sub> <sup>b</sup>	4.1, 4.0	2.2x10 <sup>-4</sup> M, 2.0x10 <sup>-4</sup> M	5x10 <sup>-5</sup> M
Water (pH <sub>0</sub> = 7, not buffered), equilibrated with SO <sub>2</sub> <sup>c</sup>	3.8	1.4x10 <sup>-4</sup>	0
Water (buffered at pH = 4), then equilibrated with SO <sub>2</sub> <sup>c</sup>	4.0	2.2x10 <sup>-4</sup>	0

<sup>a</sup> 1 ppm SO<sub>2</sub> in N<sub>2</sub> at 2 Lpm through 0.2 g deoxygenated Nuchar-SN in 200 mL degassed water.

<sup>b</sup> Experimental

<sup>c</sup> Calculated

## FIGURE CAPTIONS

Figure 1. Laboratory fog chamber and associated equipment.

Figure 2. Sulfate formation in droplets exposed to  $\text{SO}_2$  in the fog chamber.

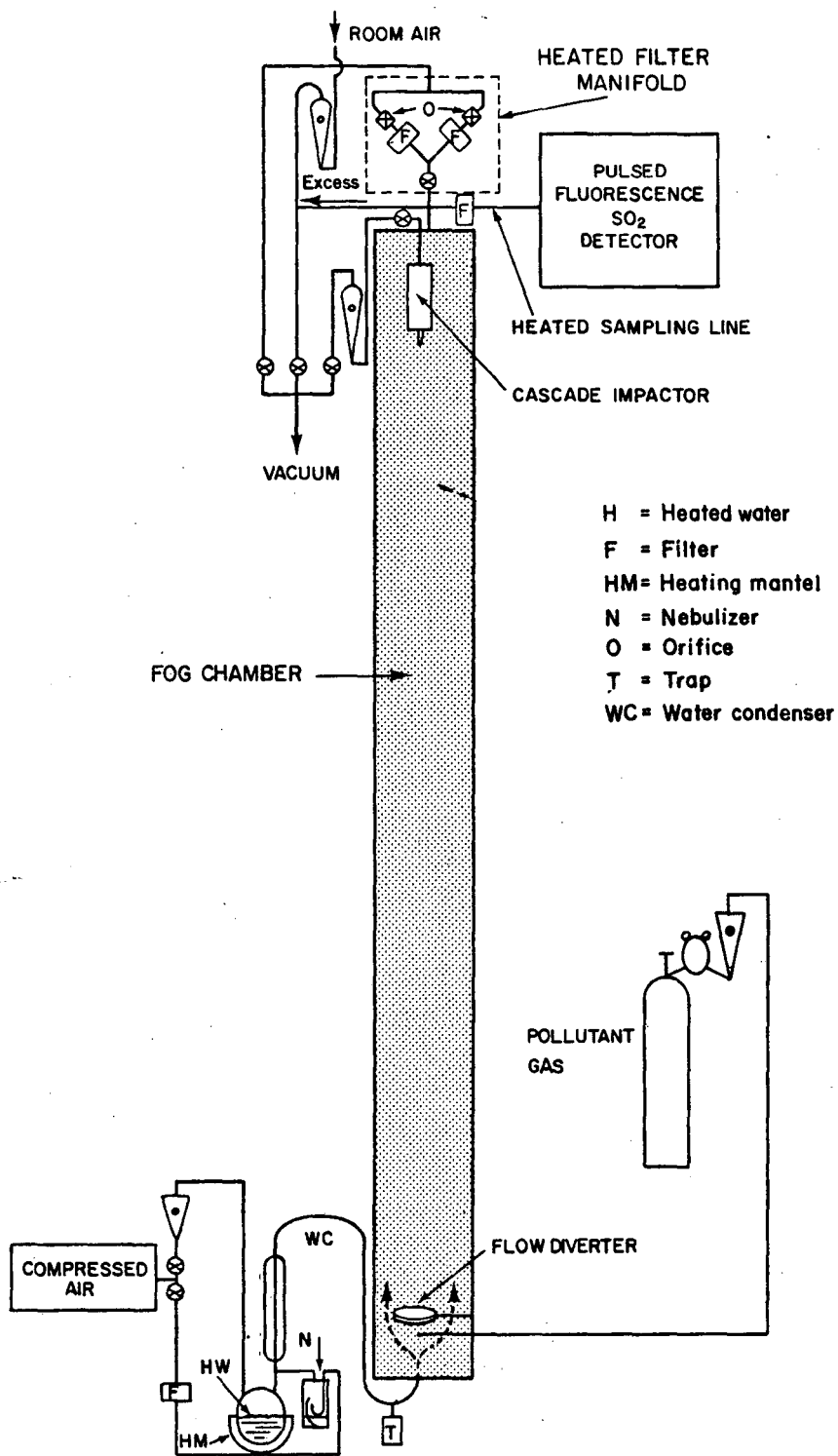
Droplets were dried by a heated filter manifold.

Figure 3. Carbon-normalized rate of sulfate formation for Nuchar droplets exposed to  $\text{SO}_2$ . Curve 1: Fog chamber droplets were dried with diffusion drier. Curve 2: Fog chamber droplets were dried by heating the filters to  $50^\circ\text{C}$ . Curve 3:  $\text{SO}_2$  in dry air was drawn through a filter ( $50^\circ\text{C}$ ) loaded with Nuchar.

Figure 4. Calculated carbon-normalized rate of sulfate formation in droplets at various pH's. (—) shows the calculated (Eq. 1) carbon-normalized rate of sulfate formation in Nuchar-containing fog droplets that are buffered at selected pH's and then equilibrated with  $\text{SO}_2$ . (---) shows the calculated (Eq. 1) carbon-normalized rate of sulfate formation for nonbuffered soot-containing fog droplets that were equilibrated with  $\text{SO}_2$  and 320 ppm  $\text{CO}_2$ . This curve is plotted using a pH-axis created by the (—) curves. Black circles are from curve 1 in Fig. 3.

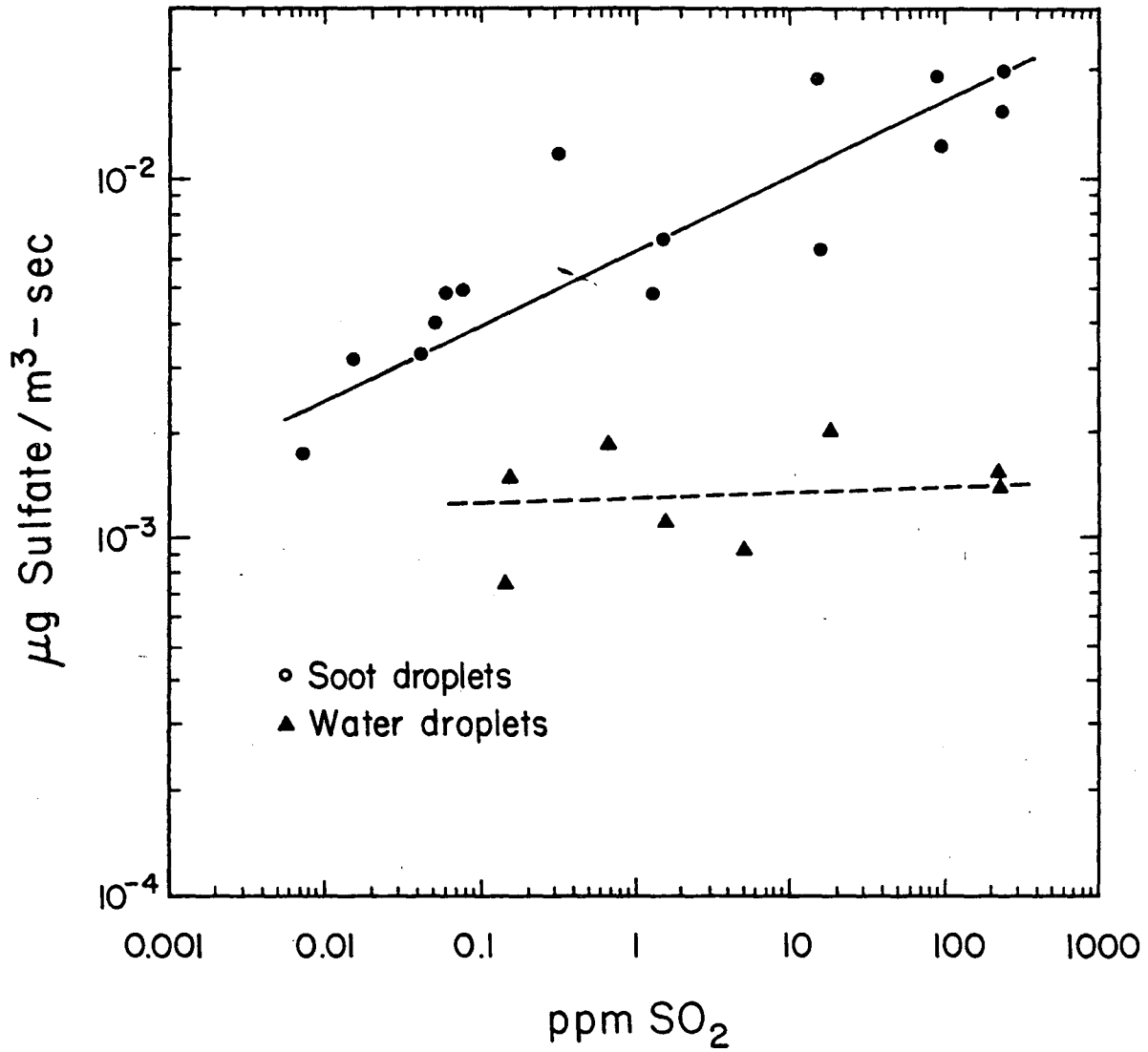
Figure 5. Titration curve of an aqueous suspension of Nuchar to which 2.0 mL of 0.1 N NaOH was added before titration to dissociate weak acids.

Figure 6. Calculated (Eq. 1) effective order (n) in  $d[\text{SO}_4^{2-}/C]/dt = k[\text{SO}_2]^n$  for several atmospheric conditions. The intersection of an  $\text{SO}_2$  curve and the line of pH due to  $\text{SO}_2$  and  $\text{CO}_2$  equilibria indicates the equilibrium pH for nonbuffered fog droplets exposed to that  $[\text{SO}_2]$  and 320 ppm  $\text{CO}_2$ .



XBL 804-4124

Figure 1



XBL-813-438

Figure 2

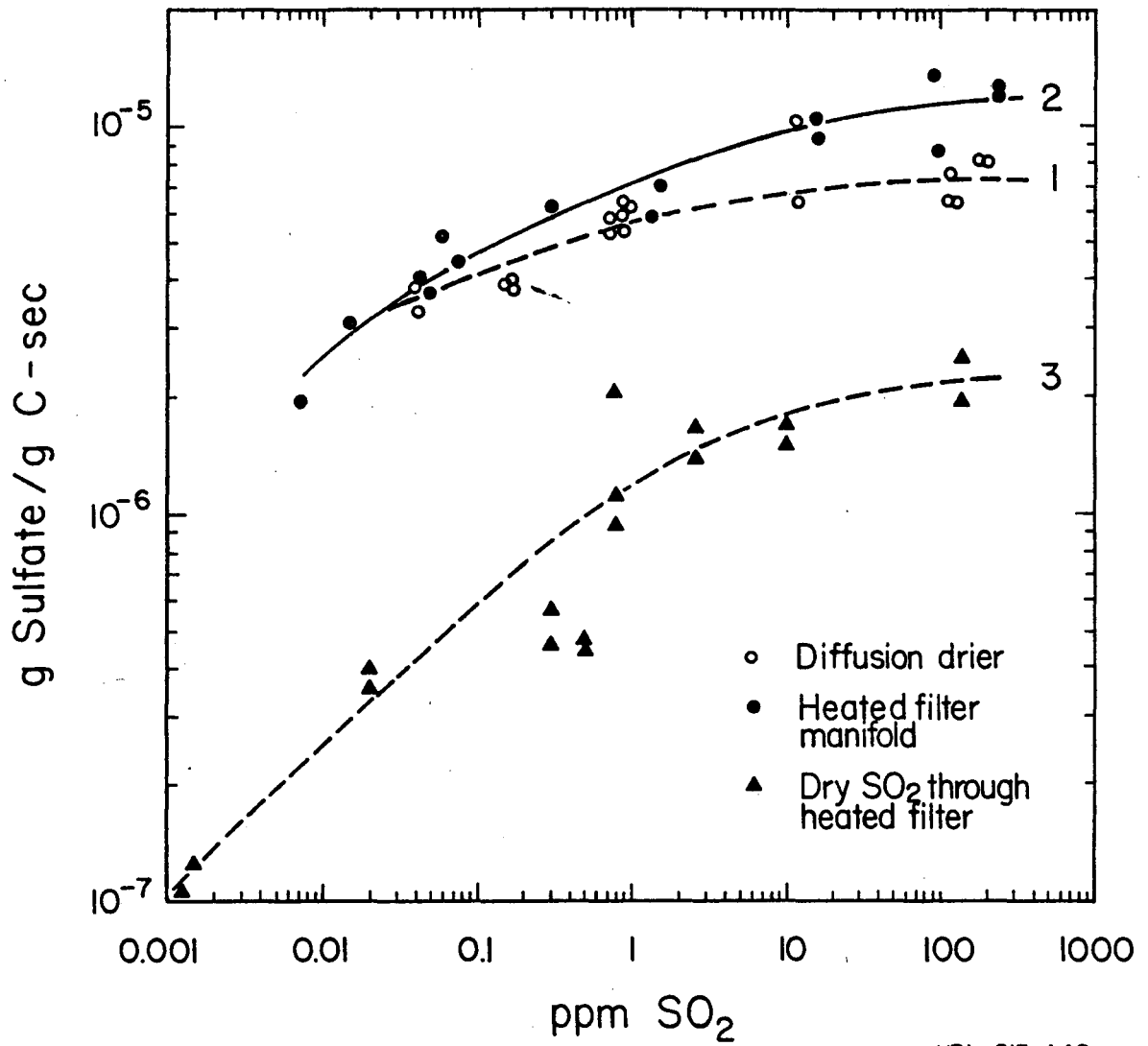
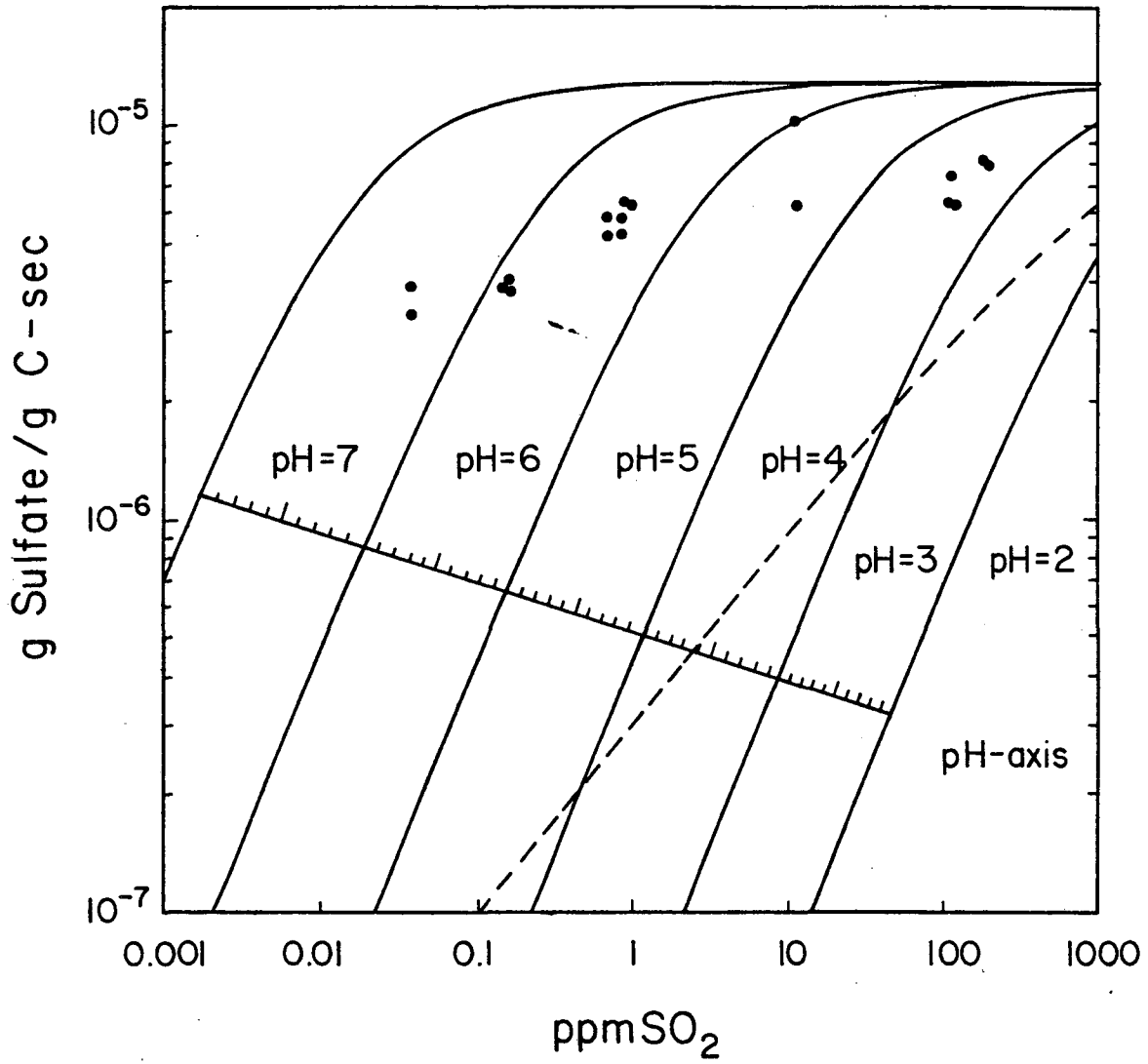


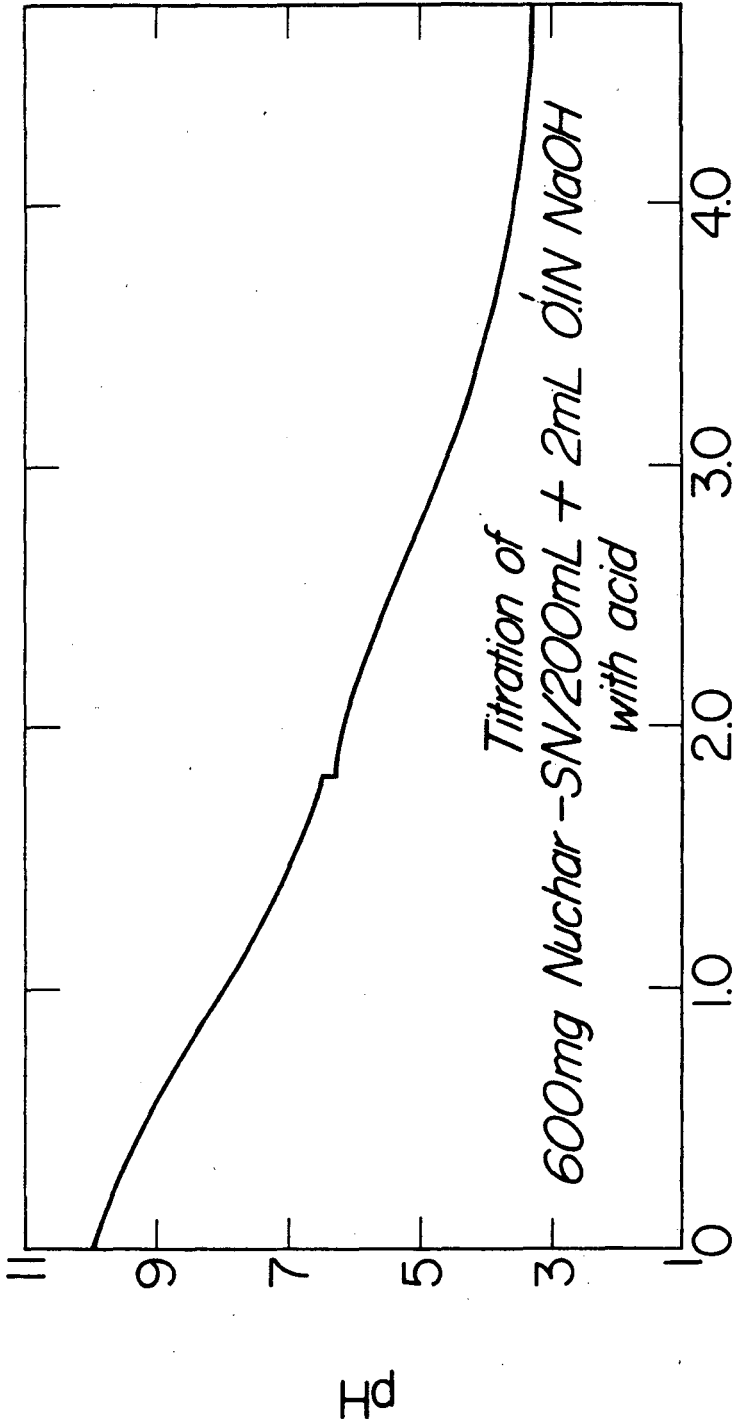
Figure 3





XBL-813-439

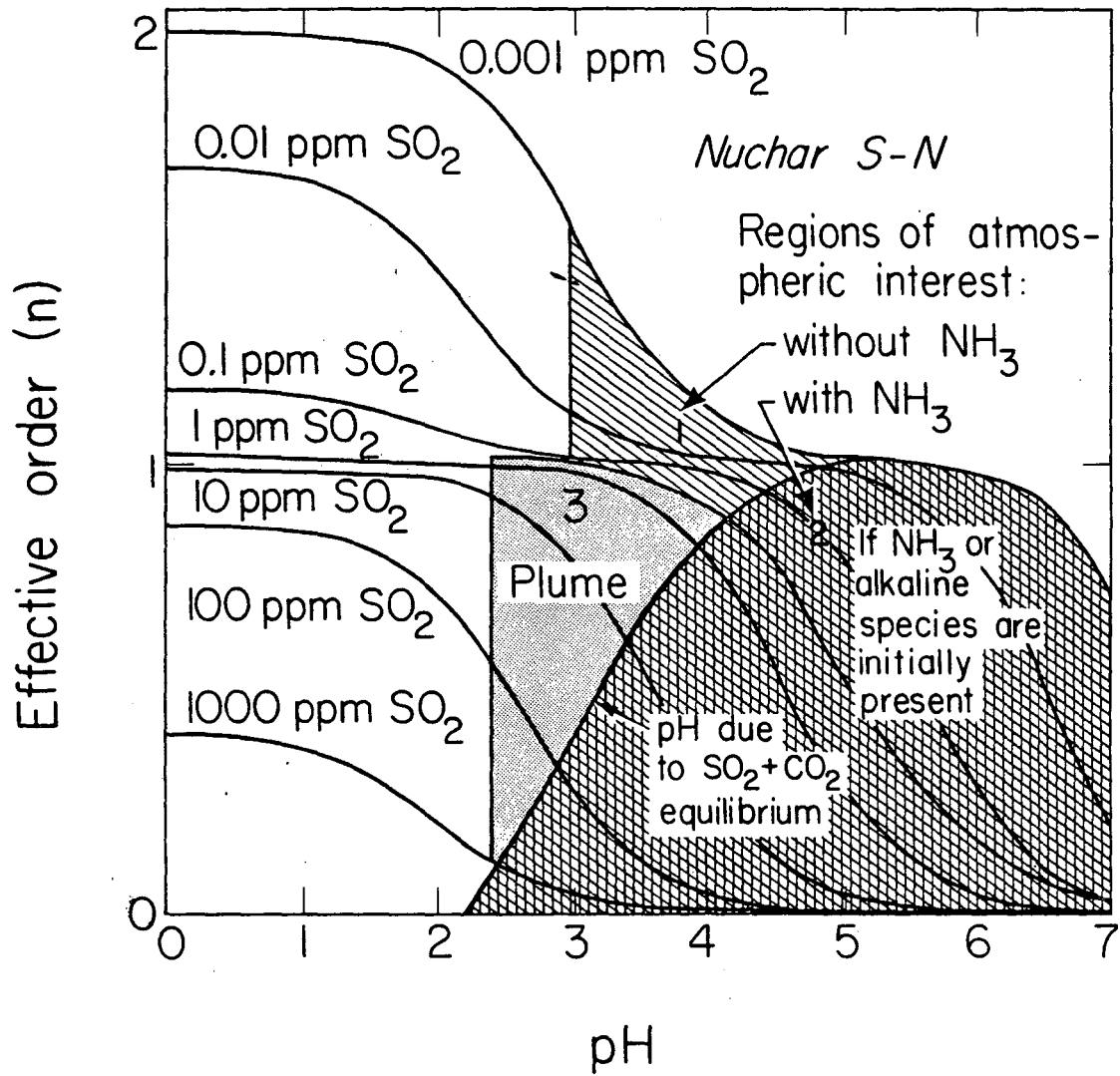
Figure 4



mL 0.1N HCl

XBL 809-1863

Figure 5



XBL 809-1862

Figure 6

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