Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

Title

THE ROLE OF SOOT PARTICLES AND NOx IN THE OXIDATION OF SO2 IN AQUEOUS SOLUTION: KINETICS, MECHANISM, AND IMPACT ON SULFATE AEROSOL FORMATION

Permalink

https://escholarship.org/uc/item/1fk4m2x0

Author

Chang, S.G.

Publication Date

2013-06-27

eScholarship.org Powered by the California Digital Library
University of California

UC-4 + 11
LBL-10886
c. 1

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

RECEIVED
LIBRARY
JUN 11 1981
LIBRARY AND
DOCUMENTS SECTION

ENERGY & ENVIRONMENT DIVISION

Presented at the U.S. Department of Energy Meeting on the Physics and Chemistry of Energy-Related Atmospheric Pollution, Harpers Ferry, WV, May 28-30, 1980

THE ROLE OF SOOT PARTICLES AND NO_x IN THE OXIDATION OF SO_2 IN AQUEOUS SOLUTION: KINETICS, MECHANISM, AND IMPACT ON SULFATE AEROSOL FORMATION

S.G. Chang, R. Brodzinsky, S. Oblath, S. Markowitz, R. Toossi, and T. Novakov

November 1980

For Reference

Not to be taken from this room

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48

LBL-10886 c.1

LEGAL NOTICE

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Lawrence Berkeley Laboratory is an equal opportunity employer.

THE ROLE OF SOOT PARTICLES AND NO_x IN THE OXIDATION OF SO_2 IN AQUEOUS SOLUTION: KINETICS, MECHANISM, AND IMPACT ON SULFATE AEROSOL FORMATION *

S.G. Chang, R. Brodzinsky, S. Oblath, S. Markowitz, R. Toossi, and T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

We have identified two previously unrecognized processes which could play an important role in terms of acid rain and sulfate aerosol formation: 1) the oxidation of SO_2 in water droplets containing soot particles, and 2) the oxidation of SO_2 by NO_x in water droplets. The results of our investigation on these two systems are outlined below.

Oxidation of SO_2 in water droplets containing soot particles. The reaction was studied by batch (flask) experiments, from which a rate law was derived.[1,2] This rate law has been confirmed by fog chamber studies.[3] The flask experiments were performed using suspensions of commercially available activated carbons as well as suspensions of combustion-produced soots. The results obtained for these different types of carbon particles show the same kinetic behavior, although the rate constants differ from type to type (Table I).

Figure 1 shows the effective rate of reaction (normalized carbon concentration, room temperature - 20°C, and air) as a function of the sulfurous acid concentration for the activated carbons studied (see also Table I). The kinetic data indicate that catalytic oxidation of SO_2 on carbon particles in aqueous solution has the following characteristics:

1. The reaction rate is independent of pH (pH < 7.6), and therefore $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-} are indistinguishable in terms of oxidation on the carbon surfaces.

2. The reaction is first order with respect to the concentration of carbon particles.

3. The activation energy of the reaction is $\sim$ 8.5 kcal/mole, being slightly different for different carbons.

4. The reaction rate has a complex dependence on the concentration of S(IV), ranging between a second and zeroth order reaction as the S(IV) concentration increases.

5. The reaction rate has a complex dependence on the concentration of dissolved O_2, with the order of reaction between zeroth and first.

Based on the experimental results, we propose the following reaction mechanism:

$$C_x + O_2(\ell) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_x \cdot O_2(\ell) \tag{1}$$

$$C_x \cdot O_2(\ell) + S(IV) \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_x \cdot O_2(\ell) \cdot S(IV) \tag{2}$$

$$C_x \cdot O_2(\ell) \cdot S(IV) + S(IV) \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} C_x \cdot O_2(\ell) \cdot 2S(IV) \tag{3}$$

$$C_x \cdot O_2(\ell) \cdot 2S(IV) \overset{k_4}{\rightarrow} C_x + 2S(VI) \tag{4}$$

where C_x = soot, $O_2(\ell)$ = dissolved oxygen molecule, S(IV) = sulfite species, and S(VI) = sulfate species.

Equation (1) indicates that dissolved oxygen is adsorbed on the soot particle surface to form an activated complex. This adsorbed oxygen complex then oxidizes the S(IV) to form sulfate according to Eqs. (2)-(4). If one assumes that the reaction follows the condition of Langmuir adsorption

equilibrium,[4] the rate of acid formation is

$$\frac{d[S(VI)]}{dt} = 2k_4[C_x] \frac{K_1[O_2]}{1+K_1[O_2]} \frac{K_2[S(IV)]}{1+K_2[S(IV)]} \frac{K_3[S(IV)]}{1+K_3[S(IV)]}, \quad \text{(I)}$$

where $K_1 = k_1/k_{-1}$, $K_2 = k_2/k_{-2}$, $K_3 = k_3/k_{-3}$.

The experimental results yield the following rate law for this reaction:

$$\frac{d[S(VI)]}{dt} = k[C_x] \frac{K[O_2]}{1+K_1[O_2]} f[S(IV)], \quad \text{(Ia)}$$

where $f[S(IV)] = \dfrac{\alpha[S(IV)]^2}{1+\beta[S(IV)]+\alpha[S(IV)]^2}$,

$[C_x]$ = grams of carbon particles per liter,

$[O_2]$ = moles of dissolved oxygen per liter, and

$[S(IV)]$ = total moles of S(IV) per liter.

Equations (I) and (Ia) are equivalent.

As mentioned previously, the rate constants of several different types of carbon particles were studied and found to differ from type to type. In principle, the reaction rate should be proportional to the concentration of carbon particles. The number of active sites per unit mass of carbon particles is different from type to type and is not necessarily proportional to the surface area. Sidelewski[5] has shown, by means of the electron paramagnetic resonance method, that free electrons on carbon particles can serve as active centers for the adsorption of oxygen molecules and for the oxidation of SO_2. The concentration of free electrons is related to the origin and thermal history of the carbon particles. It is therefore impractical to formulate a generally applicable rate constant for atmospheric soot particles because these particles may arise from the combustion of different types of fossil fuel under different

combustion conditions and may thus possess a different catalytic activity. The rate constants used in the following calculation in the assessment of the impact of this process to sulfate aerosol formation[6] represent the average value between the values of natural gas and of acetylene soot particles produced under rich flame conditions. This value is 5 times larger than that determined for Nuchar C-190 (Table I).

The dependence of the rate of formation of sulfate on the partial pressure of SO_2 (P_{SO_2}) in the atmosphere can be obtained from Eq. (Ia). Because the effect of P_{SO_2} on the rate is contained in f[S(IV)], we illustrate the relationship of f[S(IV)] with P_{SO_2} and pH of aqueous droplets as shown in Figs. 2 and 3. f[S(IV)], or the rate of production of sulfate (because the rate is linearly proportional to f[S(IV)], decreases as the pH decreases at a given P_{SO_2}. The magnitude of f[S(IV)]'s changing per unit pH change is much larger at a lower P_{SO_2}. Also f[S(IV)] (or the rate) depends only slightly on P_{SO_2} under most atmospheric conditions when P_{SO_2} is between 1 and 10 ppb and the pH ranges between 5 and 6. f[S(IV)] increases only 1/10 and twofold respectively at pH of 6 and 5 when P_{SO_2} increases from 1 to 10 ppb. However, f[S(IV)] depends strongly on P_{SO_2} when the pH is low.

<u>Oxidation of SO_2 by NO_x in water droplets.</u> Nitric and nitrous acids are produced in the aqueous phase after nitrogen oxides are absorbed into liquid water, and sulfurous acid is formed when SO_2 dissolves in water. Nitric acid reacts with sulfurous acid to form nitrosylsulfuric acid, while many concurrent and consecutive chemical reactions can occur as a result of the interaction between nitrous acid and sulfurous acid.[6] Hydroxylamine disulfonate (HADS) is the first stable product under most atmospheric conditions:

$$HNO_2 + 2HSO_3^- \rightarrow HON(SO_3)_2^{-2} + H_2O \ . \qquad (5)$$

The formation kinetic of HADS has been studied[7] in our laboratory and consists of three concurrent processes. The reaction rate law can be expressed as:

$$\frac{d[HADS]}{dt} = k_0[H^+]^2[NO_2^-] + k_I[H^+][NO_2^-][HSO_3^-] + k_{II}[NO_2^-][HSO_3^-]^2 , \qquad (II)$$

where $k_0 \approx 8 \times 10^5$ liters^2/mole-sec (at 295°K),

$k_I = 3.7 \times 10^{12}\ e^{-6100/T}$ liter^2/mole^2-sec, and

$k_{II} = 9.0 \times 10^{-4}\ e^{2.1(\mu)1/2}$ liter^2/mole^2-sec (T is temperature in Kelvin, and μ is ionic strength in moles/liter.).

$k_I[H^+][NO_2^-][HSO_3^-]$ and $k_{II}[NO_2^-][HSO_3^-]^2$ are two major processes under the conditions of the experiment (nitrite concentration, 10^{-2}-10^{-3} M; sulfite concentration, 10^{-2}-10^{-1} M; and pH, 4-7). The determination of these two processes has clarified the disagreement of previous kinetic results among Seel and Knorre,[8] Seel and Degener,[9] and Yamamoto and Kaneda.[10] In addition to these two processes, a third process, $k_0[H^+][NO_2^-]$ has been identified not only by us but also by Seel and Degener[9] and Yamamoto and Kaneda.[10] This third process was found to be independent with respect to the sulfite concentration. We tentatively assumed that this rate law will still hold in an atmosphere where concentrations of both nitrite and sulfite are several orders of magnitude lower than the concentrations used when this rate equation was derived. Therefore, a rate law which includes all three terms (Eq. II) is used in our model calculations.

HADS can undergo further reaction, either hydrolysis or sulfonation. Hydrolysis of HADS[11] produces hydroxylamine monosulfonate (HAMS) and sulfates:

$$HON(SO_3)_2^{-2} + H_2O \xrightarrow{H^+} HONHSO_3^- + HSO_4^- . \qquad (6)$$

Sulfonation of HADS[8,10] yields amine trisulfonate:

$$HON(SO_3)_2^{-2} + HSO_3^- \rightleftarrows N(SO_3)_3^{-3} + H_2O . \qquad (7)$$

The extent to which HADS will undergo hydrolysis (H) and sulfonation (S) can be represented by the following equation:

$$\frac{H}{S} = \frac{2.10\text{x}10^{11}\ e^{-17600/RT}[H^+] + 1.67\text{x}10^{11}\ e^{-23000/RT}}{3.4\text{x}10^{10}\ e^{-19200/RT}[HSO_3^-]} \quad . \qquad \text{(III)}$$

Figure 4 shows the H/S ratio against the pH of the solution at three different partial pressures of SO_2 at 25°C. Hydrolysis is more favorable at higher solution acidity, whereas sulfonation becomes more important at higher concentrations of SO_2. It is obvious that the major fraction of HADS undergoes hydrolysis under most atmospheric conditions.

If we let the rate of formation (Eq. II) equal the rate of destruction (hydrolysis), we can calculate the steady-state concentration of HADS in aqueous droplets at 295°K by the following equation:

$$[HADS]_{s.s.} = \frac{8\text{x}10^5[H^+]^2[NO_2^-] + 3.87\text{x}10^3[H^+][NO_2^-][HSO_3^-] + 9.0\text{x}10^{-4}[NO_2^-][HSO_3^-]^2}{1.92\text{x}10^{-2}[H^+] + 1.52\text{x}10^{-6}} \quad . \qquad \text{(IV)}$$

This steady-state concentration is the upper limit of HADS in aqueous droplets because the rate of destruction by way of hydrolysis will become larger than the rate of formation if the concentration of HADS is larger than this steady-state concentration. Figure 5 shows the steady-state concentration of HADS as a function of pH at two atmospheric conditions.

HAMS, a product resulting from the hydrolysis of HADS, can either undergo further hydrolysis,

$$HONHSO_3^- + H_2O \xrightarrow{H^+} NH_3OH^+ + SO_4^{-2} \quad , \qquad (8)$$

or react with nitrous acid to produce nitrous oxide and sulfates,

$$HONHSO_3^- + HNO_2 \xrightarrow{H^+} N_2O\uparrow + HSO_4^- + H_2O \ . \tag{9}$$

Although a complete rate law has not been determined for both reactions, indications from the kinetic study[11,12] are that the reaction with nitrous acid is much more important than the hydrolysis. Therefore, it appears that the reaction between SO_2 and HNO_2 in atmospheric water droplets will first produce HADS (5), which undergoes acid-catalyzed hydrolysis to form HAMS and sulfate (6). HAMS then reacts with nitrous acid and ends up as nitrous oxide and sulfate (9). The total stoichiometric equation can be expressed as

$$2HNO_2 + 2HSO_3^- \rightarrow N_2O\uparrow + 2HSO_4^- + H_2O \ . \tag{10}$$

If the reaction is at steady-state condition, then two moles of sulfate will be produced — (6) and (9) — for every mole of HADS consumed (or produced), assuming that the reaction rate between HAMS and nitrous acid is very large.

Comparison of sulfate production mechanisms. We have carried out a box-type calculation to compare the relative importance of sulfate production mechanisms by soot particles and nitrous acid with other mechanisms involving liquid water. The systems considered in the batch reactor include the SO_2-CO_2-$H_2O(\ell)$-air and any of the oxidizing agents such as O_2, O_3, HNO_2, or catalysts such as Fe^{+++}, Mn^{++}, and soot. The role of NH_3 is investigated in these reactions. The kinetics of each of these processes other than soot-catalyzed and HNO_2 reactions have been studied by many investigators. The results of Beilke et al.,[13] Erickson et al.,[14] Freiberg,[15] and Matteson et al.[16] for oxygen, ozone, iron, and manganese systems respectively were used in this calculation.

All the oxidation mechanisms considered except Mn^{++} are pH dependent. Most of these mechanisms have lower oxidation rates at a lower pH, but some are more sensitive to the change in pH than others. The HNO_2 mechanism shows

a larger oxidation rate when the solution is more acidic, however. The following initial conditions were used in the calculation: liquid water, 0.05 g/m^3; SO_2, 0.01 ppm; O_3, 0.05 ppm; and CO_2, 0.000311 atm. Concentrations of particulate Fe and Mn of 250 ng/m^3 and 20 ng/m^3 respectively were assumed. However, only 0.13% of the total iron and 0.25% of the manganese are water soluble, according to Gordon et al.[17] The concentrations of soot and HNO_2 were taken as 10 $\mu g/m^3$ and 8 ppb respectively. The latter corresponds to 25 ppb of NO and 50 ppb of NO_2 at equilibrium conditions.[18] For NH_3 a concentration of 5 ppb was used, which is higher than the highest equilibrium partial pressure of NH_3 over the United States as calculated by Lau and Charlson.[19] Tables II and III list the equilibrium equations and oxidation rate equations used for this comparative study.

The following assumptions were made in the calculations:

1. The size of liquid water drops suspended inside the box is so small that the absorption rate of gaseous species (SO_2, NH_3, and HNO_2) is governed by chemical reactions.

2. There is no mass transfer of any species across the box during the reaction; therefore, the SO_2 (and NH_3 or HNO_2) in each box is depleted with time. The mass balance of the SO_2, CO_2, NH_3, and HNO_2 is always maintained (i.e., $\Delta[SO_2]g = \Delta[SO_2 \cdot H_2O] + \Delta[HSO_3^-] + \Delta[SO_3^{-2}] + \Delta[HSO_4^-] + \Delta[SO_4^{-2}]$; $\Delta[CO_2]g = \Delta[CO_2 \cdot H_2O] + \Delta[HCO_3^-] + \Delta[CO_3^{-2}]$; $\Delta[NH_3]g = \Delta[NH_3 \cdot H_2O] + \Delta[NH_4^+]$; and $\Delta[HNO_2]g = \Delta[HNO_2] + \Delta[NO_2^-] + 2\Delta[N_2O]g$; all units are in mole).

3. The growth of liquid water droplets due to the vapor pressure lowering effect of the sulfuric acid formed in the droplets is neglected.

The rate of sulfate production is determined by a calculation scheme involving a combination of equilibrium and kinetic steps. Equilibrium between SO_2 in the gas phase and sulfur (IV) in the droplet is several orders of magnitude faster than oxidation of sulfur (IV) to sulfate.[20] Similar assumptions

were made regarding NH_3 and CO_2 gases. Therefore, initially gases are taken to be in equilibrium with the aerosols. Then the formation of sulfate proceeds by the given time-dependent production rate. The increase in the sulfate level in the small time step Δt causes the reduction in pH of the solution, which in turn disturbs the equilibrium between the aerosol and its surrounding gaseous environment. More gases are dissolved in the aerosol to maintain the equilibrium. At the same time, these gases are depleted in the surrounding atmosphere. After each calculation, the time step is adjusted and the process is repeated until a 24-hour period is completed. The results are shown in Fig. 6, indicating that O_3, soot, and HNO_2 can be important mechanisms for sulfate aerosol formation. In general the O_3 mechanism is more important under high pH and/or photoactivity conditions when the concentration of O_3 is high, whereas both soot and HNO_2 processes are more important when the lifetime of fog or clouds is long and the pH of the droplets is low. Both soot and HNO_2 processes can be dominant processes close to sources and in heavily polluted urban areas, where the concentrations of soot and NO/NO_2 are high and the pH of aqueous droplets is low.

The rate constant for atmospheric soot particles varies depending on the nature and history of particle production as discussed previously. In a fog chamber study, Benner et al.[3] have recently found that the reaction rate of soot particles from a natural gas diffusion flame can be considerably faster than the reaction rate reported here. More determination of rate constants of soot from different types of fuel is therefore warranted.

The chemistry of reactions between SO_2 and HNO_2 in aqueous solution is very complicated. Many concurrent and consecutive chemical reactions can occur as indicated previously. Because of the unavailability of a complete kinetic study, we have ignored the sulfate contribution from at least two

additional concurrent pathways that can occur as a result of the reaction between HNO_2 and sulfites. These two pathways are 1) the hydrolysis of nitrosulfonic acid,[21] an intermediate resulting from the interaction of HNO_2 and sulfites to hyponitrous acid and sulfate; and 2) the reaction of nitrosulfonic acid with HNO_2[22] to produce NO and sulfate. A complete understanding of the kinetics of these two pathways and a confirmation on the validity of rate equation (2) of hydroxylamine disulfonate formation at a much lower concentration of nitrites and sulfites are needed before one can finally assess the extent of contribution this system can make in terms of atmospheric sulfate aerosol and acid rain formation.

Acknowledgment. This work was supported by the Assistant Secretary for the Environment, Office of Health and Environmental Research, Pollutant Characterization and Safety Research Division. of the U.S. Department of Energy under Contract No. W-7405-ENG-48.

References

1. S.G. Chang, R. Brodzinsky, R. Toossi, S.S. Markowitz, and T. Novakov, Proceedings, Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory Report LBL-9037, p. 122 (1979).
2. R. Brodzinsky, S.G. Chang, S.S. Markowitz, and T. Novakov, Lawrence Berkeley Laboratory Report LBL-10488; accepted for publication in J. Phys. Chem. (1980).
3. W.H. Benner, private communication, Lawrence Berkeley Laboratory (1979).
4. A. Clark, The Theory of Adsorption and Catalysis, New York, Academic (1970).
5. J. Siedlewski, Int. Chem. Eng. 5, 297 (1965).
6. S.G. Chang, R. Toossi, and T. Novakov, Lawrence Berkeley Laboratory Report LBL-11380; accepted for publication in Atmos. Environ. (1980).
7. S.B. Oblath, S.S. Markowitz, T. Novakov, and S.G. Chang, Lawrence Berkeley Laboratory Report LBL-10504; accepted for publication in J. Phys. Chem. (1980).
8. V.F. Seel and H. Knorre, Z. anorg. allg. Chem. 313, 70 (1961).
9. V.F. Seel and E. Degener, Z. anorg. allg. Chem. 284, 101 (1956).
10. S. Yamamoto and T. Kaneda, Nippon Kagaku Zasshi 80, 1098 (1959).
11. S. Naiditch and D.M. Yost, J. Am. Chem. Soc. 63, 2123 (1941).
12. V.F. Seel and H. Pauschmann, Z. Naturforschg. 17b, 347 (1962).
13. S. Beilke, D. Lamb, and J. Müller, Atmos. Environ. 9, 1083 (1975).
14. R.E. Erickson, L.M. Yates, R.L. Clark, and D. McEwen, Atmos. Environ. 11, 813 (1977).
15. J. Freiberg, Atmos. Environ. 9, 661 (1975).
16. M.J. Matteson, W. Stöber, and H. Luther, Ind. & Eng. Chem. Fundam. 8, 677 (1969).
17. G.E. Gordon, D.D. Davis, G.W. Israel, H.E. Landsberg, and T.C. O'Haver, Report NSF/RA/E-73/189 (1975); available from NTIS as PB 262 574.

18. S.E. Schwartz and W.H. White, Brookhaven National Laboratory Report BNL27102 (1980).

19. N.C. Lau and R.J. Charlson, Atmos. Environ. 11, 475 (1977).

20. S. Beilke and G. Gravenhorst, Atmos. Environ. 14, 463 (1978).

21. W. Latimer and J.H. Hildebrand, Reference Book of Inorganic Chemistry, New York, Macmillan, p. 208 (1951).

22. F. Raschig, Schwefel und Stickstoffstudien, Berlin, Verlag Chemie (1924).

Table I. Summary of kinetic data for the catalytic oxidation of SO_2 by various elemental carbon particles in aqueous suspension.

Reaction rate equation:

$$\frac{d[SO_4^{-2}]}{dt} = Ae^{-Ea/RT} [C_x] \left\{ \frac{K_1 [O_2]}{1 + K_1 [O_2]} \right\} \left\{ \frac{\alpha [S(IV)]^2}{1 + \beta [S(IV)] + \alpha [S(IV)]^2} \right\}$$

Kinetic data \ Elemental carbon	Nuchar C-190 (WESVACO)	Nuchar SN (WESVACO)	Aktivkohle (MERCK)
A (moles/g-sec)	0.874	0.158	2.473
E_a (kcal/mole)	8.8	8.1	8.8
K_1 (ℓ/mole)	2.103×10^3	7.427×10^3	4.372×10^3
α (ℓ^2/mole^2)	2.404×10^{12}	4.915×10^8	9.519×10^{11}
β (ℓ/mole)	1.219×10^7	2.956×10^5	3.738×10^7

Table II. Chemical equilibrium constants at 25°C.

$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^-$	$K_2 = 1.0008\times10^{-14}$
$CO_2(g) + H_2O(\ell) \overset{H_c}{\rightleftharpoons} CO_2 \cdot H_2O$	$H_c = 3.4\times10^{-2}$
$CO_2 \cdot H_2O \overset{K_{1c}}{\rightleftharpoons} HCO_3^- + H^+$	$K_{1c} = 4.45\times10^{-7}$
$HCO_3^- \overset{K_{2c}}{\rightleftharpoons} CO_3^{-2} + H^+$	$K_{2c} = 4.68\times10^{-11}$
$NH_3(g) + H_2O(\ell) \overset{H_a}{\rightleftharpoons} NH_3 \cdot H_2O$	$H_a = 57$
$NH_3 \cdot H_2O \overset{K_a}{\rightleftharpoons} NH_4^+ + OH^-$	$K_a = 1.774\times10^{-5}$
$SO_2(g) + H_2O(\ell) \overset{H_s}{\rightleftharpoons} SO_2 \cdot H_2O$	$H_s = 1.24$
$SO_2 \cdot H_2O \overset{K_{1s}}{\rightleftharpoons} HSO_3^- + H^+$	$K_{1s} = 1.7\times10^{-2}$
$HSO_3^- \overset{K_{2s}}{\rightleftharpoons} SO_3^{-2} + H^+$	$K_{2s}' = 6.24\times10^{-8}$
$HSO_4^- \overset{K_{3s}}{\rightleftharpoons} H^+ + SO_4^{-2}$	$K_{3s} = 1.2\times10^{-2}$
$HNO_2(g) + H_2O \overset{H_N}{\rightleftharpoons} HNO_2 \cdot H_2O$	$H_N = 5.1\times10^{-4}$
$HNO_2 \cdot H_2O \overset{K_N}{\rightleftharpoons} H^+ + NO_2^-$	$K_N = 5.1\times10^{-4}$
$O_2 + H_2O \overset{H_{O_2}}{\rightleftharpoons} O_2 \cdot H_2O$	$H_{O_2} = 1.08\times10^{-3}$
$O_3 + H_2O \overset{H_{O_3}}{\rightleftharpoons} O_3 \cdot H_2O$	$H_{O_3} = 1.23\times10^{-2}$

[a]Concentrations in moles/ℓ and gas pressure in atm.

Table III. Rate of SO_2 oxidation by various mechanisms in aqueous droplets.

Mechanism	Reaction rate law[a]
O_2	$\text{Rate} = \dfrac{H_S \{k_2 + k_{10}K_W/[H^+]\}\ K_{2S}k_3}{k_{-2}[H^+]^2 + k_{-10}[H^+] + K_{2S}k_3} P_{SO_2}$
O_3	$\text{Rate} = \{k_4[HSO_3^-] + k_5[SO_3^{-2}]\}\ [O_3 \cdot H_2O]$
Fe^{+++}	$\text{Rate} = \dfrac{k_0 k_S^2 H_S^2 P_{SO_2}^2 [Fe^{+++}]}{[H^+]^3}$
Mn^{++}	$\text{Rate} = 3.67\text{x}10^{-3}[X] - 1.17\ \{[HSO_4^-] + [SO_4^{-2}]\}^2 \{[Mn^{++}] - [X]\}\ x[H_2O(\ell)]^{-2}$
	$\text{where } X = \dfrac{k_1 H_S P_{SO_2}[Mn^{++}]}{k_1\{H_S P_{SO_2} + [H_2O(\ell)][Mn^{++}]\} + 0.17}$
Soot	$\text{Rate} = k_6[C_x][O_2]^{.69} \dfrac{\alpha[S^{+4}]^2}{1 + \beta[S^{+4}] + \alpha[S^{+4}]^2}$
HNO_2	$\text{Rate} = k_7[H^+]^2[NO_2^-] + k_8[H^+][NO_2^-][HSO_3^-] + k_9[NO_2^-][HSO_3^-]^2$

[a] $[H_2O(\ell)]$ in cc/m^3, concentration in mole/ℓ, gas pressure in atm, and time in sec, k_0 = 151.69 ℓ/mole-sec, $k_S = 1.84\text{x}10^{-2}$ mole/ℓ, $k_1 = 8.12\text{x}10^4$ ℓ/mole-sec, $k_2 = 3.4\text{x}10^6\ sec^{-1}$; $k_{-2} = 2\text{x}10^8$ ℓ/mole-sec, $k_{10} = 2.9\text{x}10^5$ ℓ/mole-sec, $k_{-10} = 2.3\text{x}10^{-7}\ sec^{-1}$, $k_3 = 1.7\text{x}10^{-3}\ sec^{-1}$, $k_4 = 1.1\text{x}10^5$ ℓ/mole-sec, $k_5 = 7.4\text{x}10^8$ ℓ/mole-sec, $k_6 = 1.2\text{x}10^{-4}\ mole^{.3} \cdot \ell^{.7}/g \cdot sec$, $\alpha = 1.5\text{x}10^{12}\ \ell^2/mole^2$, $\beta = 3.06\text{x}10^6$ ℓ/mole, $k_7 = 8\text{x}10^5\ \ell^2/mole^2\text{-sec}$, $k_8 = 3.8\text{x}10^3\ \ell^2/mole^2\text{-sec}$, $k_9 = 9\text{x}10^{-4}\ \ell^2/mole^2\text{-sec}$.

Figure Captions

Figure 1. Effective rate of oxidation of S(IV) catalyzed on various activated carbon particles vs. S(IV) concentration.

Figure 2. The effect of the pH of aqueous droplets on f[S(IV)] at P_{SO_2} = 100, 10, and 1 ppb. f[S(IV)] is a function of S(IV) that the aqueous oxidation rate of sulfites on soot particles depends on.

Figure 3. The effect of partial pressure of SO_2 on f[S(IV)] at pH of 7, 6, 5, 4, and 3. f[S(IV)] is a function of S(IV) that the aqueous oxidation rate of sulfites on soot particles depends on.

Figure 4. The ratio of the rate of hydrolysis (H) to sulfonation (S) of hydroxylamine disulfonate as a function of the pH of aqueous droplets at P_{SO_2} = 1 ppb, 10 ppb, and 1 ppm.

Figure 5. The steady-state concentration of hydroxylamine disulfonate in aqueous droplets as a function of pH at two atmospheric conditions: $P_{SO_2} = P_{NO_2} = 2P_{NO}$ = 10 ppb, and $P_{SO_2} = P_{NO_2} = 2P_{NO}$ = 1 ppb.

Figure 6. Comparison of the relative importance of various sulfate production mechanisms involving liquid water based on a box-type calculation. The following initial conditions were used in the calculation: P_{SO_2} = 0.01 ppm; P_{CO_2} = 0.000311 atm; P_{NH_3} = 5 ppb; P_{O_3} = 0.05 ppm; P_{HNO_2} = 8 ppb; $[Fe^{+3}]$ = 1.2×10^{-7} mole/ℓ; $[Mn^{+2}]$ = 1.8×10^{-8} mole/ℓ; soot = 10 μg/m^3; and liquid water = 0.05 g/m^3.

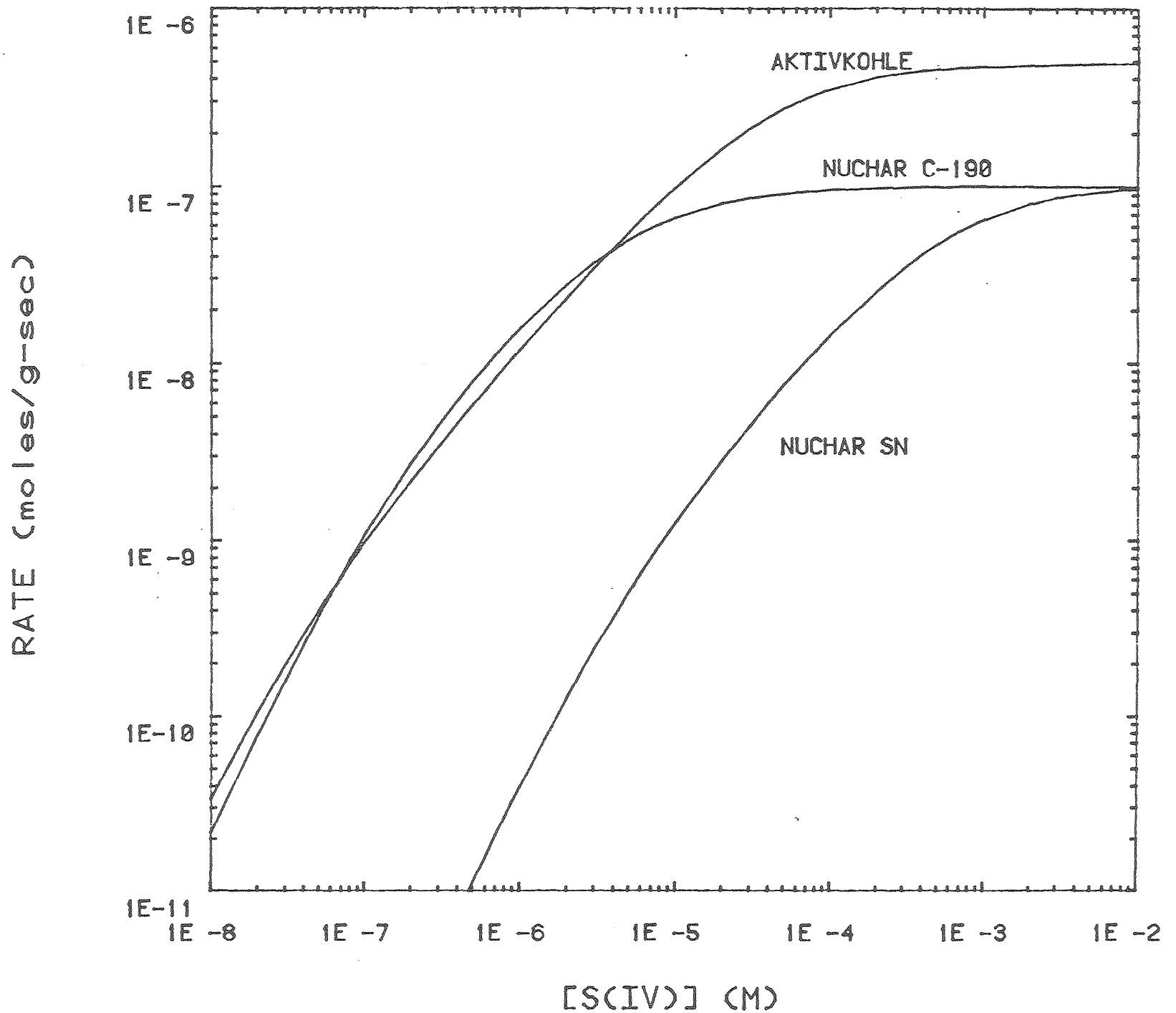

AKTIVKOHLE
NUCHAR C-190
NUCHAR SN
RATE (moles/g-sec)
1E -6
1E -7
1E -8
1E -9
1E-10
1E-11
1E -8
1E -7
1E -6
1E -5
1E -4
1E -3
1E -2
[S(IV)] (M)

Figure 1.

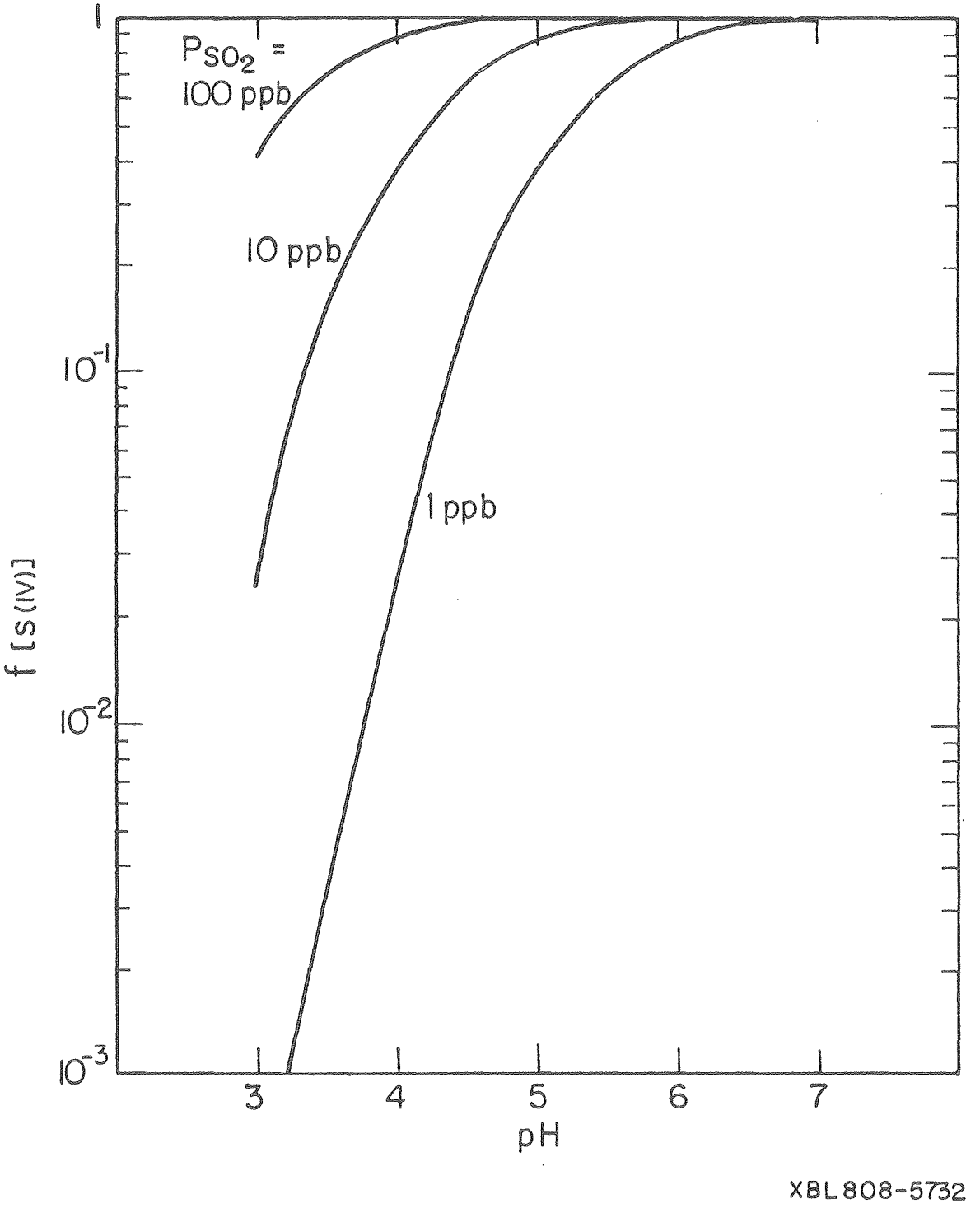

1
10^{-1}
10^{-2}
10^{-3}
f [S(IV)]
P_{SO_2} =
100 ppb
10 ppb
1 ppb
3
4
5
6
7
pH
XBL 808-5732

Figure 2.

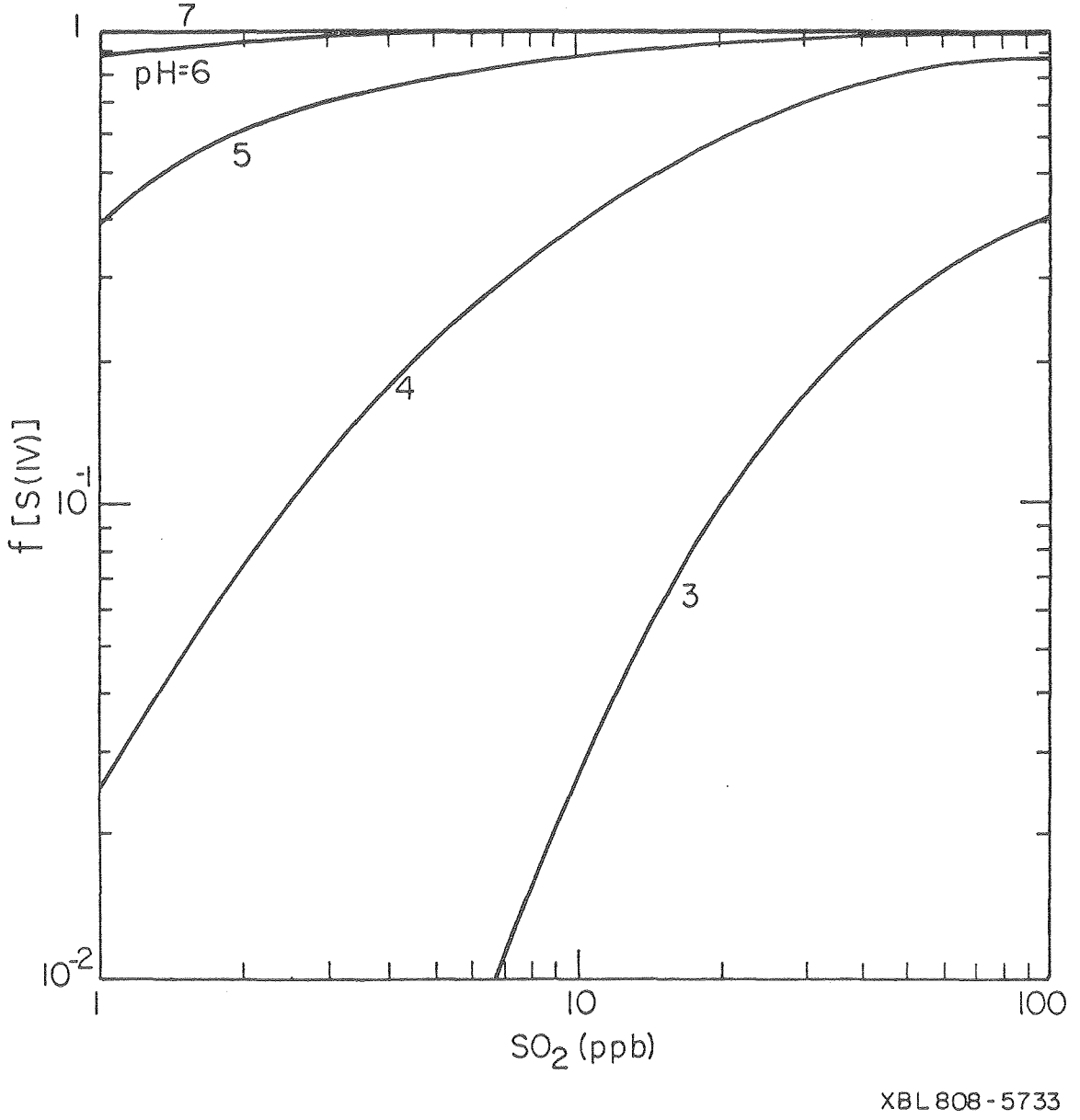


Figure 3.

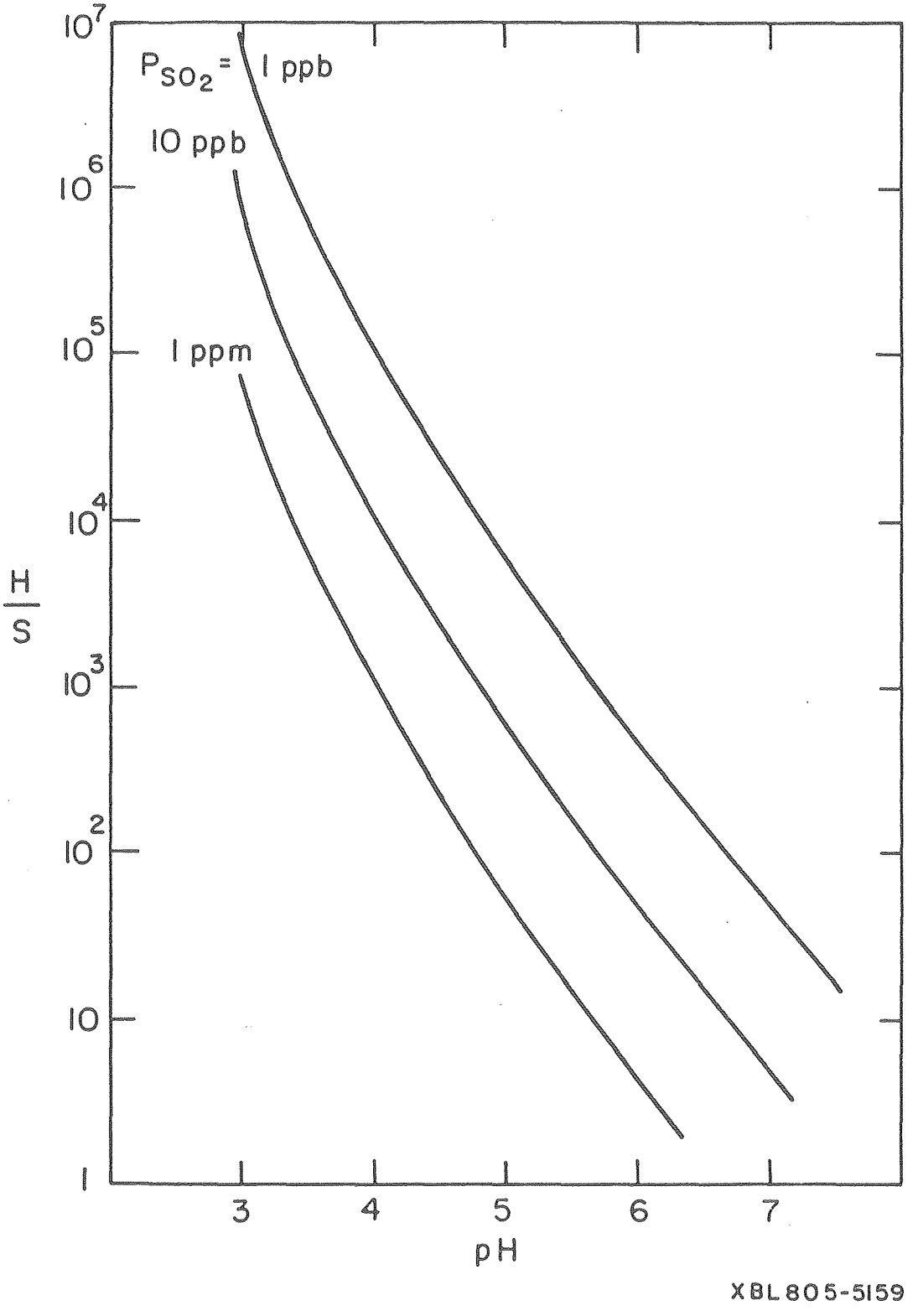
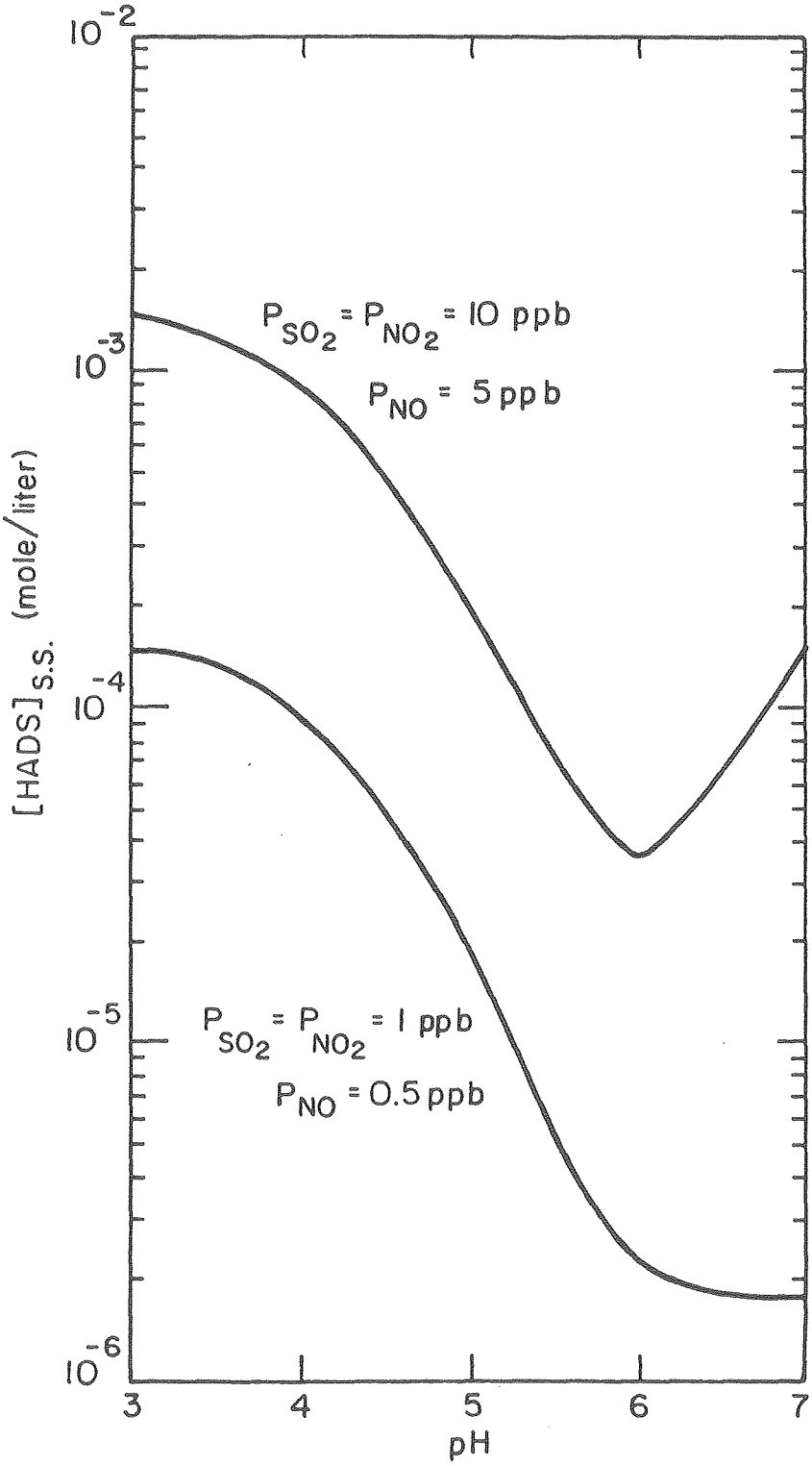

10^7
10^6
10^5
10^4
10^3
10^2
10
1
H/S
P_{SO_2} = 1 ppb
10 ppb
1 ppm
3
4
5
6
7
pH
XBL805-5159

Figure 4.



XBL 808-7334

Figure 5.

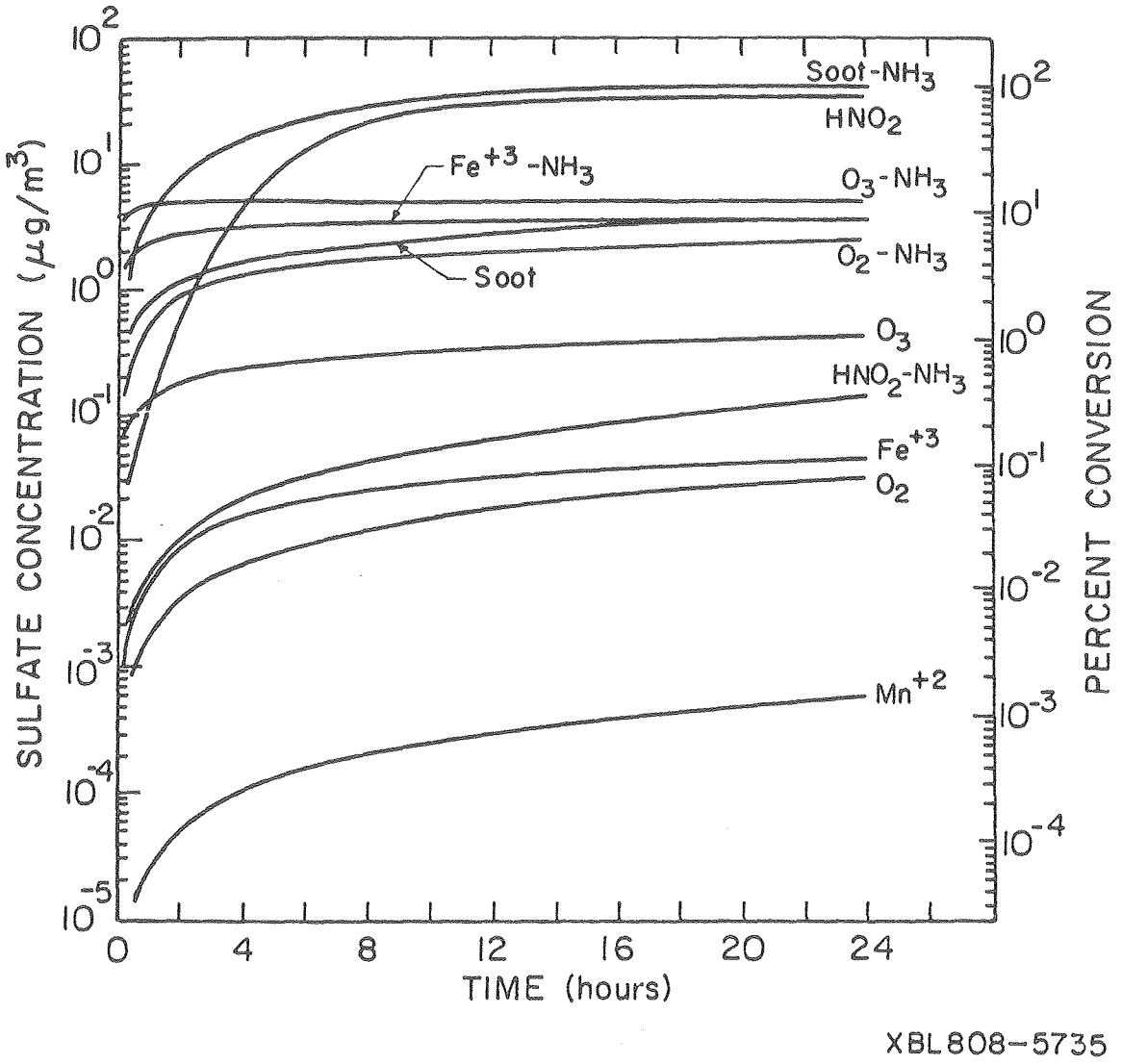

SULFATE CONCENTRATION (μg/m³)
PERCENT CONVERSION
TIME (hours)
Soot-NH3
HNO2
Fe+3-NH3
O3-NH3
O2-NH3
Soot
O3
HNO2-NH3
Fe+3
O2
Mn+2
XBL808-5735

Figure 6.

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720