Lawrence Berkeley National Laboratory
Recent Work

Title

THE IMPORTANCE OF SOOT PARTICLES AND NITROUS ACID IN OXIDIZING SO2 IN ATMOSPHERIC AQUEOUS DROPLETS

Permalink

https://escholarship.org/uc/item/9r2947tv

Authors

Chang, S.G.
Toossi, R.
Novakov, T.

Publication Date

1980-09-01

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

LBL-11380 c.2
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

ENERGY & ENVIRONMENT DIVISION

Submitted to Atmospheric Environment

THE IMPORTANCE OF SOOT PARTICLES AND NITROUS ACID IN OXIDIZING SO_2 IN ATMOSPHERIC AQUEOUS DROPLETS

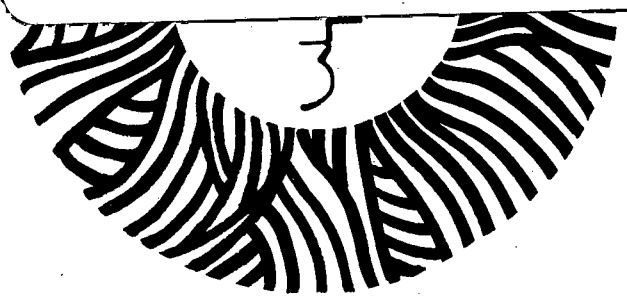
S.G. Chang, R. Toossi, and T. Novakov

September 1980

RECEIVED
LAWRENCE
BERKELEY LABORATORY
NOV 6 1980
LIBRARY AND
DOCUMENTS SECTION

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782.



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

LBL-11380 c.2

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

THE IMPORTANCE OF SOOT PARTICLES AND NITROUS ACID IN OXIDIZING SO_2 IN ATMOSPHERIC AQUEOUS DROPLETS

S.G. Chang, R. Toossi, and T. Novakov

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

Soot particles catalyze the oxidation of $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-} species at the same rate; however, the rate of production of sulfate is not constant at a constant partial pressure of SO_2. The rate decreases as the pH decreases because the total concentration of S(IV) in aqueous droplets decreases as the pH decreases. The sulfate production rate has a complex dependence on the concentration of S(IV) and is not very sensitive to a change in SO_2 concentration at normal atmospheric conditions.

The oxidation of SO_2 by HNO_2 in atmospheric water droplets first produces hydroxylamine disulfonate, which undergoes acid-catalyzed hydrolysis to form sulfate and hydroxylamine monosulfonate. The latter can react with HNO_2 and would then end up as nitrous oxide and sulfate.

Model calculations have been made comparing the relative importance of the sulfate production mechanism by soot particles and nitrous acid with other mechanisms involving liquid water. The results indicate that both soot and HNO_2 mechanisms can be very important when the lifetime of the atmospheric aqueous droplets is long.

Introduction

Atmospheric sulfate, a major constituent in ambient aerosol particles, is presumably formed by the oxidation of SO_2. The dominant mechanisms responsible for this transformation have not yet been established. One set of mechanisms thought to be important involves the dissolution of SO_2 in water droplets. When liquid water is present — as in clouds, fog, and plumes — the atmospheric SO_2 can dissolve in the droplets and be oxidized to sulfate. Aqueous oxidation mechanisms involving trace metal catalysts such as Fe^{+3} and Mn^{+2} and oxidizing species like O_2, O_3, and H_2O_2 have been studied and compared (Beilke and Gravenhorst, 1978; Chang et al., 1978; Hegg and Hobbe, 1978; Middleton et al., 1980; Penkett et al., 1979). We have recently identified two previously unrecognized mechanisms which could play an important role in terms of sulfate aerosol formation: 1) oxidation of SO_2 in water droplets containing soot particles (Chang et al., 1978; Brodzinsky et al., 1980), and 2) oxidation of SO_2 by HNO_2 in water droplets (Oblath et al., 1980).

This paper discusses the implications of the kinetic results of these two systems on atmospheric aerosol formation and presents the results of a model calculation which compares the relative importance of various sulfate production mechanisms involving liquid water.

Review of Previous Results

1. Oxidation of SO_2 in water droplets containing soot particles. Soots that were produced by the combustion of acetylene and natural gas and from a diesel engine were used in the kinetic study and showed the same reaction characteristics as those obtained by suspensions of similar concentrations of activated carbon (Nuchar C-190). Since it is difficult to reproducibly prepare soot suspensions, suspensions of Nuchar were used as a model system. The majority of results are therefore obtained from the model system. The kinetic

data indicate that catalytic oxidation of SO_2 on soot 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 carbon surfaces; 2) the reaction rate is first order and 0.69^{th} order with respect to the concentration of carbon and dissolved oxygen respectively; 3) 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; and 4) the activation energy of the reaction is 11.7 kcal/mole. The reaction rate law can be expressed by the following equation:

$$\frac{d[S(VI)]}{dt} = k[C_x][O_2]^{0.69} f[S(IV)] , \qquad (1)$$

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

$[C_x]$ = grams of carbon particles/L,

$[O_2]$ = moles of dissolved oxygen/L, and

$[S(IV)]$ = total moles of S(IV)/L.

The rate constants for Nuchar C-190 were determined as follows:

$k = 9.04 \times 10^3 \; e^{-5888/T}$ moles$^{.31} \cdot$L$^{.69}$/g$\cdot$sec (T is temperature in Kelvin.),

$\alpha = 1.50 \times 10^{12}$ L^2/mole^2, and

$\beta = 3.06 \times 10^6$ L/mole.

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. (1). 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 the aqueous droplets as shown in Figs. 1 and 2. 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.

The catalytic oxidation of sulfurous acid on carbon particles of different origins shows the same kinetic behavior. However, 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 active sites on the carbon particles, rather than 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 (1965) 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 erroneous to conclude a rate constant for atmospheric soot particles in general because these particles may arise from the combustion of different types of fossil fuel under different combustion conditions and thus possess a different catalytic activity. The rate constants used in these calculations represent the average value between the values of natural gas and of acetylene soot particles produced under rich flame conditions. This value (pre-exponential factor in Eq. [1]) is five times larger than that determined for Nuchar C-190.

2. Oxidation of SO_2 by HNO_2 in water droplets. Many concurrent and consecutive chemical reactions can occur as a result of the interaction between

nitrous acid and sulfurous acid (Raschig, 1924; Latimer and Hildebrand, 1951; Duecker and West, 1959). Hydroxylamine disulfonate (HADS) is the first stable product under most atmospheric conditions:

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

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

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

where $k_0 \approx 8\times10^5$ liters^2/mole-sec (at 295°K),

$k_I = 3.7\times10^{12}\ e^{-6100/T}$ liter^2/mole^2-sec, and

$k_{II} = 9.0\times10^{-4}\ e^{2.1(\mu)^{1/2}}$ 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 (1961), Seel and Degener (1956), and Yamamoto and Kaneda (1959). 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 (1956), and Yamamoto and Kaneda (1959). 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. 2) is used in our model calculations.

HADS can undergo further reaction, either hydrolysis or sulfonation. Hydrolysis of HADS (Naiditch and Yost, 1941) produces hydroxylamine monosulfonate (HAMS) and sulfates:

$$HON(SO_3)^{-2} + H_2O \xrightarrow{H^+} HONOHSO_3^- + HSO_4^- \qquad (b)$$

Sulfonation of HADS (Yamamoto and Kaneda, 1959; Seel and Knorre, 1961) yields amine trisulfonate:

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

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

$$\frac{H}{S} = \frac{2.10\times10^{11}\ e^{-17600/RT}[H^+] + 1.67\times10^{11}\ e^{-23000/RT}}{3.4\times10^{10}\ e^{-19200/RT}[HSO_3^-]} \qquad (3)$$

Figure 3 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. 2) 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:

$$[HADS]_{s.s.} = \frac{8\times10^5[H^+]^2[NO_2^-] + 3.87\times10^3[H^+][NO_2^-][HSO_3^-] + 9.0\times10^{-4}[NO_2^-][HSO_3^-]^2}{\left\{1.92\times10^{-2}[H^+] + 1.52\times10^{-6}\right\}} \qquad (4)$$

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 4 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,

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

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

$$HONHSO_3^- + HNO_2 \xrightarrow{H^+} N_2O\uparrow + HSO_4^- + H_2O \quad . \qquad (e)$$

Although a complete rate law has not been determined for both reactions, indications from the kinetic study (Naiditch and Yost, 1941; Seel and Pauschmann, 1962) 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 (a), which undergoes acid-catalyzed hydrolysis to form HAMS and sulfate (b). HAMS then reacts with nitrous acid and ends up as nitrous oxide and sulfate (e). The total stoichiometric equation can be expressed as

$$2HNO_2 + 2HSO_3^- \rightarrow N_2O\uparrow + 2HSO_4^- + H_2O \quad . \qquad (f)$$

If the reaction is at steady-state condition, then two moles of sulfate will be produced (b and e) 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. (1975), Erickson et al. (1977), Freiberg (1975), and Matteson et al. (1969) 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. (1975). 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 (Schwartz and White, 1980). 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 (1977). Tables 1 and 2 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 (Beilke and Gravenhorst, 1977). 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. 1.

Fig. 4 indicates 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

of O_3 is high, whereas both soot and HNO_2 processes are more important when the lifetime of fog or clouds is long (Toossi et al., 1980) 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. (1979) 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 (Latimer and Hildebrand, 1951), 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 (Raschig, 1924) 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 Biomedical and Environmental Research Division of the U.S. Department of Energy (Contract No. W-7405-Eng-48).

References

Beilke S. and Gravenhorst G. (1978) Heterogeneous SO_2 oxidation in the droplet phases. Atmos. Environ. 14, 463-472.

Beilke S., Lamb D. and Müller J. (1975) On the uncatalyzed oxidation of atmospheric SO_2 by oxygen in aqueous systems. Atmos. Environ. 9, 1083-1090.

Benner W.H. (1979) Private communication (Lawrence Berkeley Laboratory).

Brodzinsky R., Chang S.G., Markowitz S.S. and Novakov T. (1980) Kinetics and mechanism for the catalytic oxidation of sulfur dioxide on carbon in aqueous suspensions. Accepted for publication in J. Phys. Chem.

Chang S.G., Brodzinsky R., Toossi R., Markowitz S.S. and Novakov T. (1979) Catalytic oxidation of SO_2 on carbon in aqueous suspensions. Proc. Conference on Carbonaceous Particles in the Atmosphere, Lawrence Berkeley Laboratory Report LBL-9037, pp. 122-130.

Duecker W. and West J., eds. (1959) The manufacture of sulfuric acid. Am. Chem. Soc. Monograph Series No. 144.

Erickson R.E., Yates L.M., Clark R.L. and McEwen D. (1977) The reaction of sulfur dioxide with ozone in water and its possible atmospheric significance. Atmos. Environ. 11, 813-817.

Freiberg J. (1975) The mechanism of iron catalyzed oxidation of SO_2 in oxygenated solutions. Atmos. Environ. 9, 661-673.

Gordon, G.E., Davis D.D., Israel G.W., Landsberg H.E. and O'Haver T.C. (1975) Atmospheric impact of major sources and consumers of energy. NSF/RA/E-75/189 (available from NTIS as PB 262 574).

Hegg D.A. and Hobbs P.V. (1978) Oxidation of sulfur dioxide in aqueous systems with particular reference to the atmosphere. Atmos. Environ. 12, 241-253.

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

Lau N.C. and Charlson R.J. (1977) On the discrepancy between background atmospheric ammonia gas measurements and the existence of acid sulfates as a dominant atmospheric aerosol. Atmos. Environ. 11, 475-478.

Matteson M.J., Stöber W. and Luther H. (1969) Kinetics of the oxidation of sulfur dioxide by aerosols of manganese sulfate. Ind. & Eng. Chem. Fundam. 8, 677-687.

Middleton P., Kiang, C.S. and Mohnen V.A. (1980) Theoretical estimates of the relative importance of various urban sulfate aerosol production mechanisms. Atmos. Environ. 14, 463-472.

Naiditch S. and Yost D.M. (1941) The rate and mechanism of the hydrolysis of hydroxylamine disulfonate ion. J. Am. Chem. Soc. 63, 2123-2127.

Oblath S.B., Markowitz S.S., Novakov T. and Chang S.G. (1980) Kinetics of the formation of hydroxylamine disulfonate by reaction of nitrite with sulfites. Accepted for publication in J. Phys. Chem.

Penkett S.A., Jones B.M.R., Brice K.A. and Eggleton A.E.J. (1979) The importance of atmospheric ozone and hydrogen peroxide in oxidising sulphur dioxide in cloud and rainwater. Atmos. Environ. 13, 123-137.

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

Seel V.F. and Degener E. (1956) Kinetik und Chemismus der Raschigschen hydroxylamin-synthese. Z. anorg. allg. Chem. 284, 101-130.

Seel V.F. and Knorre H. (1961) Die Umsetzung von Nitrit mit Hydrogensulfit in Hydrogensulfit-sulfit-pufferlösungen. Z. anorg. allg. Chem. 313, 70-89.

Seel V.F. and Pauschmann H. (1962). Zum Kinetic der Umsetzung von Hydroxylaminemonosulfonat mit Nitrit. Z. Naturforschg. 17b, 347-349.

Siedlewski J. (1965) The mechanism of catalytic oxidation on activated carbon; The influence of free carbon radicals on the adsorption of SO_2. Int. Chem. Eng. 5, 297-301.

Toossi R., Chang S.G., and Novakov T. (1979) Lifetime of liquid water drops in ambient air: Consideration of the effects of surfactants and chemical reactions. Lawrence Berkeley Laboratory Report LBL-8696, pp. 149-161.

Yamamoto S. and Kaneda T. (1959) Kinetics of formation of hydroxylamine disulfonate and nitrilosulfonate by Raschig's hydroxylamine process. Nippon Kagaku Zasshi 80, 1098-1102.

*Schwartz S.E. and White W.H. (1980) Equilibrium solubility of the nitrogen oxides and oxyacids in aqueous solution. Brookhaven National Laboratory BNL27102.

Table 1. Chemical equilibrium constants at 25°C.[a]

$H_2O \overset{K_w}{\rightleftharpoons} H^+ + OH^-$	$K_2 = 1.0008\times10^{-14}$
$CO_2(g) + H_2O(\ell) \overset{H_c}{\rightleftharpoons} CO_2\cdot H_2O$	$H_c = 3.4\times10^{-2}$
$CO_2\cdot H_2O \overset{K_{1c}}{\rightleftharpoons} HCO_3^- + H^+$	$K_{1c} = 4.45\times10^{-7}$
$HCO_3^- \overset{K_{2c}}{\rightleftharpoons} CO_3^{-2} + H^+$	$K_{2c} = 4.68\times10^{-11}$
$NH_3(g) + H_2O(\ell) \overset{H_a}{\rightleftharpoons} NH_3\cdot H_2O$	$H_a = 57$
$NH_3\cdot H_2O \overset{K_a}{\rightleftharpoons} NH_4^+ + OH^-$	$K_a = 1.774\times10^{-5}$
$SO_2(g) + H_2O(\ell) \overset{H_s}{\rightleftharpoons} SO_2\cdot H_2O$	$H_s = 1.24$
$SO_2\cdot H_2O \overset{K_{1s}}{\rightleftharpoons} HSO_3^- + H^+$	$K_{1s} = 1.7\times10^{-2}$
$HSO_3^- \overset{K_{2s}}{\rightleftharpoons} SO_3^{-2} + H^+$	$K_{2s} = 6.24\times10^{-8}$
$HSO_4^- \overset{K_{3s}}{\rightleftharpoons} H^+ + SO_4^{-2}$	$K_{3s} = 1.2\times10^{-2}$
$HNO_2(g) + H_2O \overset{H_N}{\rightleftharpoons} HNO_2\cdot H_2O$	$H_N = 5.1\times10^{-4}$
$HNO_2\cdot H_2O \overset{K_N}{\rightleftharpoons} H^+ + NO_2^-$	$K_N = 5.1\times10^{-4}$
$O_2 + H_2O \overset{H_{O2}}{\rightleftharpoons} O_2\cdot H_2O$	$H_{O2} = 1.08\times10^{-3}$
$O_3 + H_2O \overset{H_{O3}}{\rightleftharpoons} O_3\cdot H_2O$	$H_{O3} = 1.23\times10^{-2}$

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

Table 2. Rate of SO_2 oxidation by various mechanisms in aqueous droplets.

Mechanism	Reaction rate law[a]
O_2	$\text{Rate} = \frac{H_S \left\{ k_2 + k_{10} K_W / [H^+] \right\} K_{2S} k_3}{k_{-2}[H^+]^2 + k_{-10}[H^+] + K_{2S} k_3} P_{SO_2}$
O_3	$\text{Rate} = \left\{ k_4 [HSO_3^-] + k_5 [SO_3^{-2}] \right\} [O_3 \cdot H_2O]$
Fe^{+++}	$\text{Rate} = \frac{k_0 k_S^2 H_S^2 P_{SO_2}^2 [Fe^{+++}]}{[H^+]^3}$
Mn^{++}	$\text{Rate} = 3.67\text{x}10^{-3}[X] - 1.17 \left\{ [HSO_4^-] + [SO_4^{-2}] \right\}^2 \left\{ [Mn^{++}] - [X] \right\} \text{x} [H_2O(\ell)]^{-2}$
	where $X = \frac{k_1 H_S P_{SO_2} [Mn^{++}]}{k_1 \left\{ H_S P_{SO_2} + [H_2O(\ell)] [Mn^{++}] \right\} + 0.17}$
Soot	$\text{Rate} = k_6 [C_x] [O_2]^{.69} \frac{\alpha [S^{+4}]^2}{1 + \beta [S^{+4}] + \alpha [S^{+4}]^2}$
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, $k_7 = 8\text{x}10^5$ $\ell^2/mole^2$-sec, $k_8 = 3.8\text{x}10^3$ $\ell^2/mole^2$-sec, $k_9 = 9\text{x}10^{-4}$ $\ell^2/mole^2$-sec.

Figure 1. 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 2. 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 3. 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 4. 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 5. 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; $[Fe^{+3}] = 1.2 \times 10^{-7}$ mole/ℓ; $[Mn^{+2}] = 1.8 \times 10^{-8}$ mole/ℓ; soot = 10 μg/m^3; and liquid water = 0.05 g/m^3.

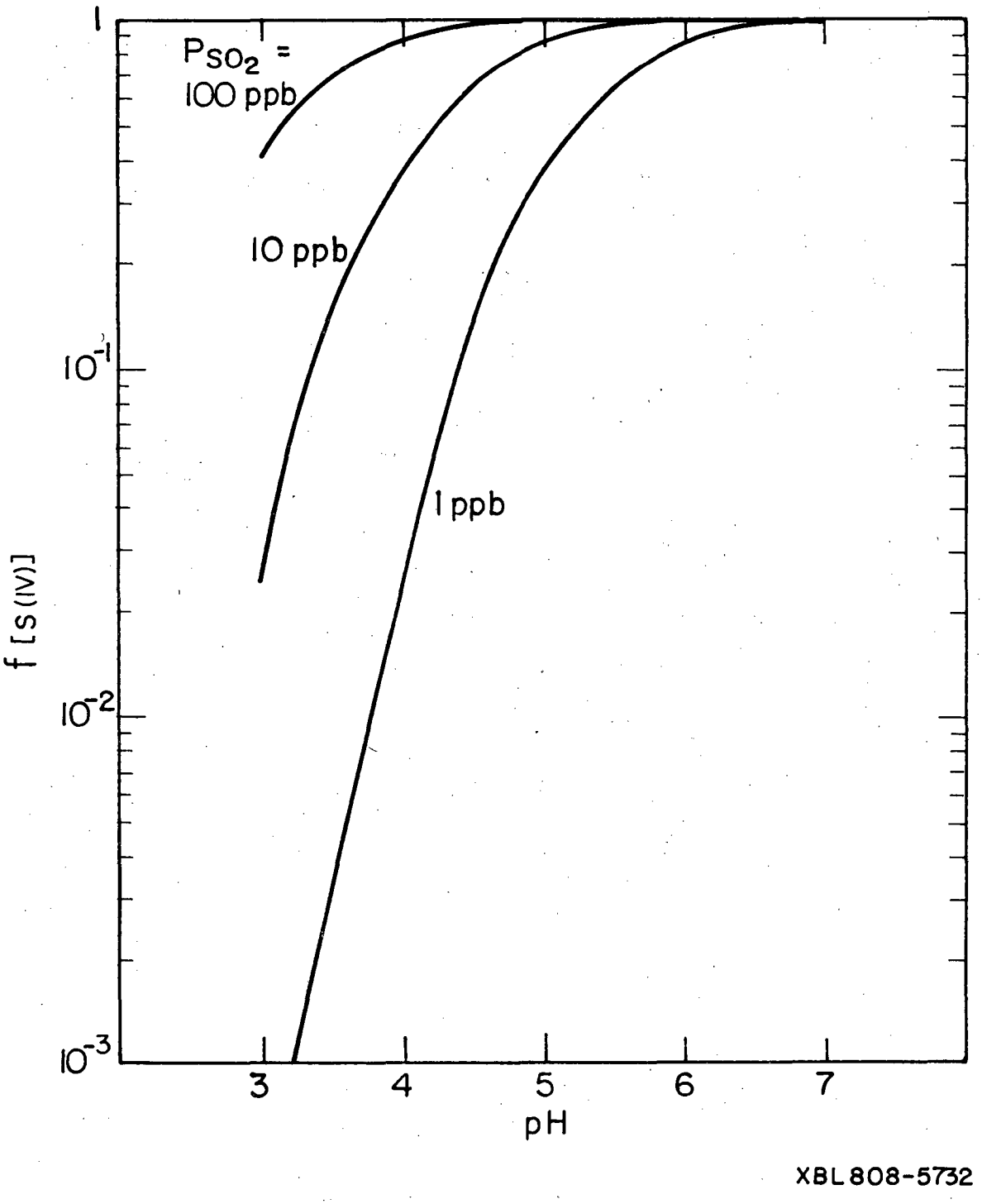

1
P_{SO_2} =
100 ppb
10 ppb
1 ppb
10^{-1}
10^{-2}
10^{-3}
f [S(IV)]
3
4
5
6
7
pH
XBL808-5732

Figure 1

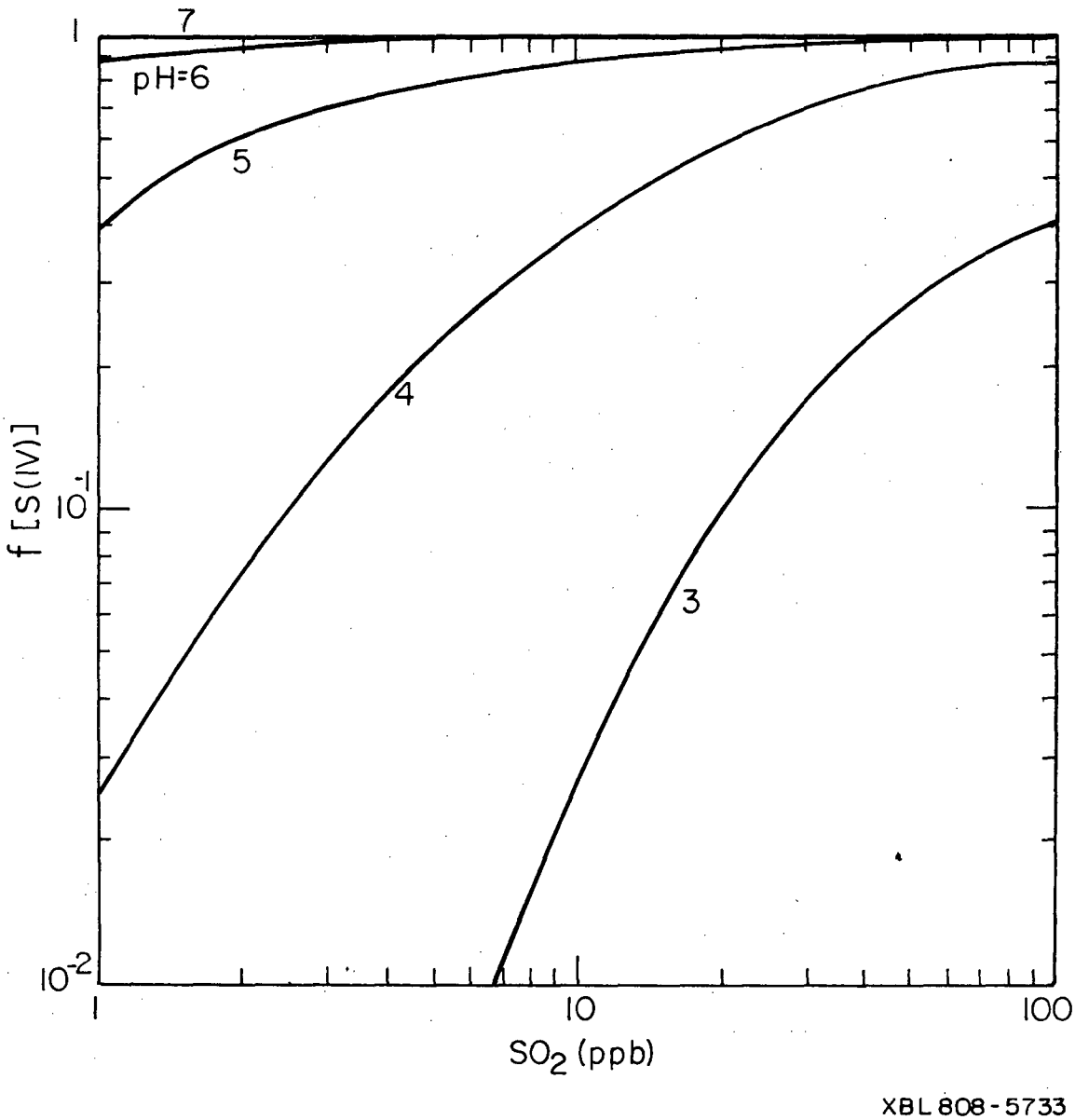


Figure 2

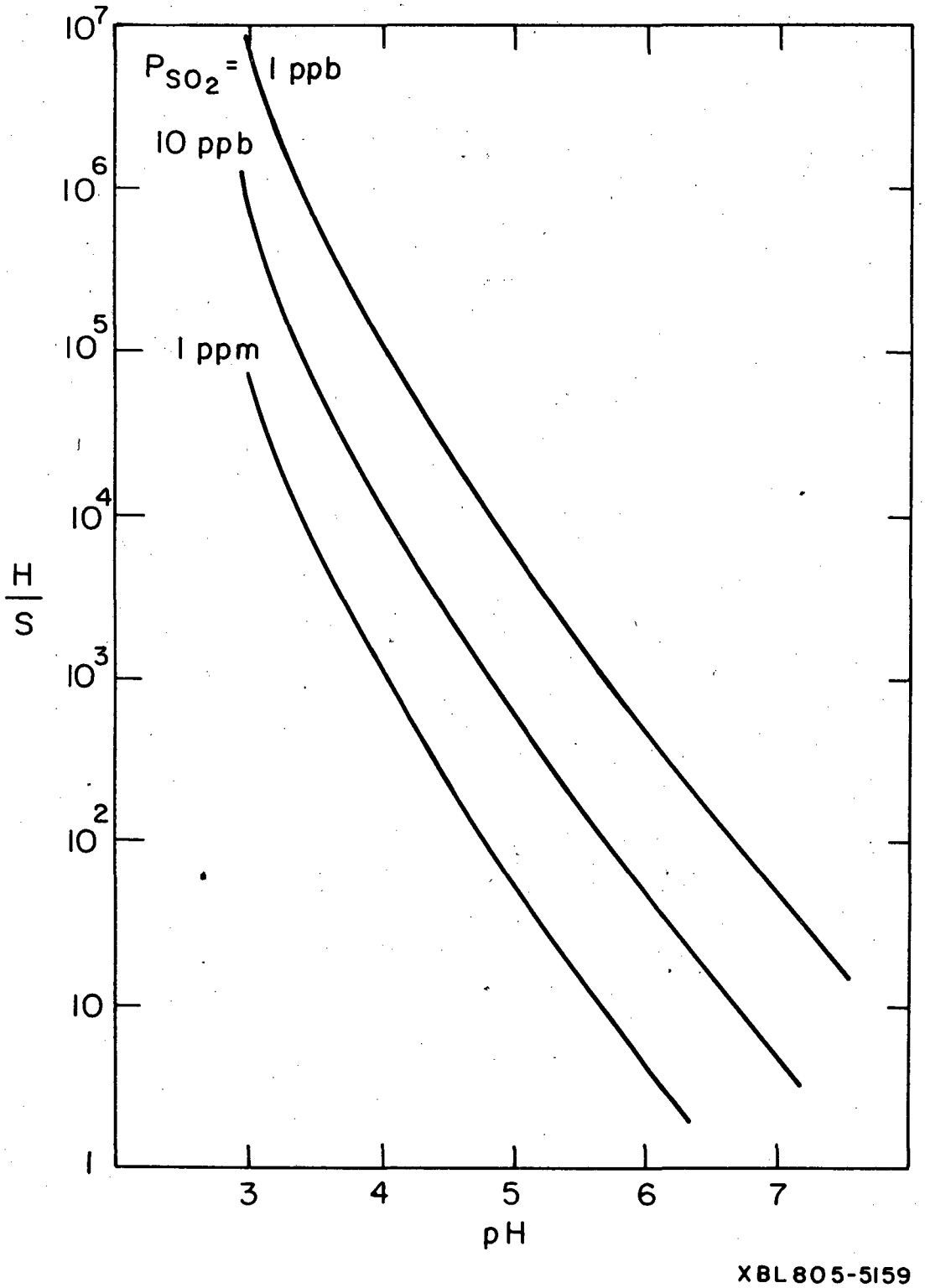

10^7
P_{SO_2} = 1 ppb
10 ppb
10^6
10^5
1 ppm
10^4
H/S
10^3
10^2
10
1
3
4
5
6
7
pH
XBL805-5159

Figure 3

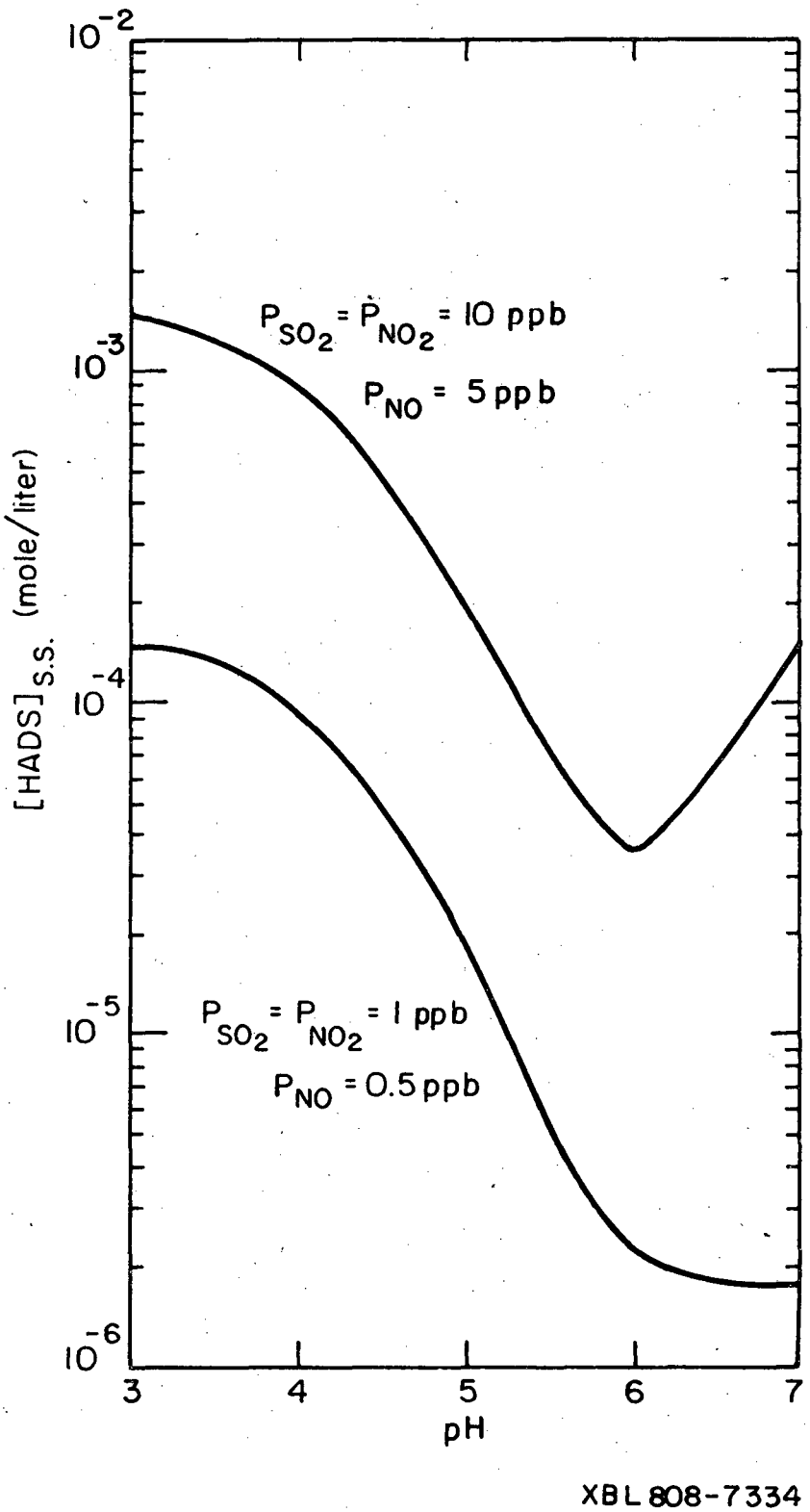

10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
$[HADS]_{s.s.}$ (mole/liter)
$P_{SO_2} = P_{NO_2} = 10$ ppb
$P_{NO} = 5$ ppb
$P_{SO_2} = P_{NO_2} = 1$ ppb
$P_{NO} = 0.5$ ppb
3
4
5
6
7
pH
XBL 808-7334

Figure 4

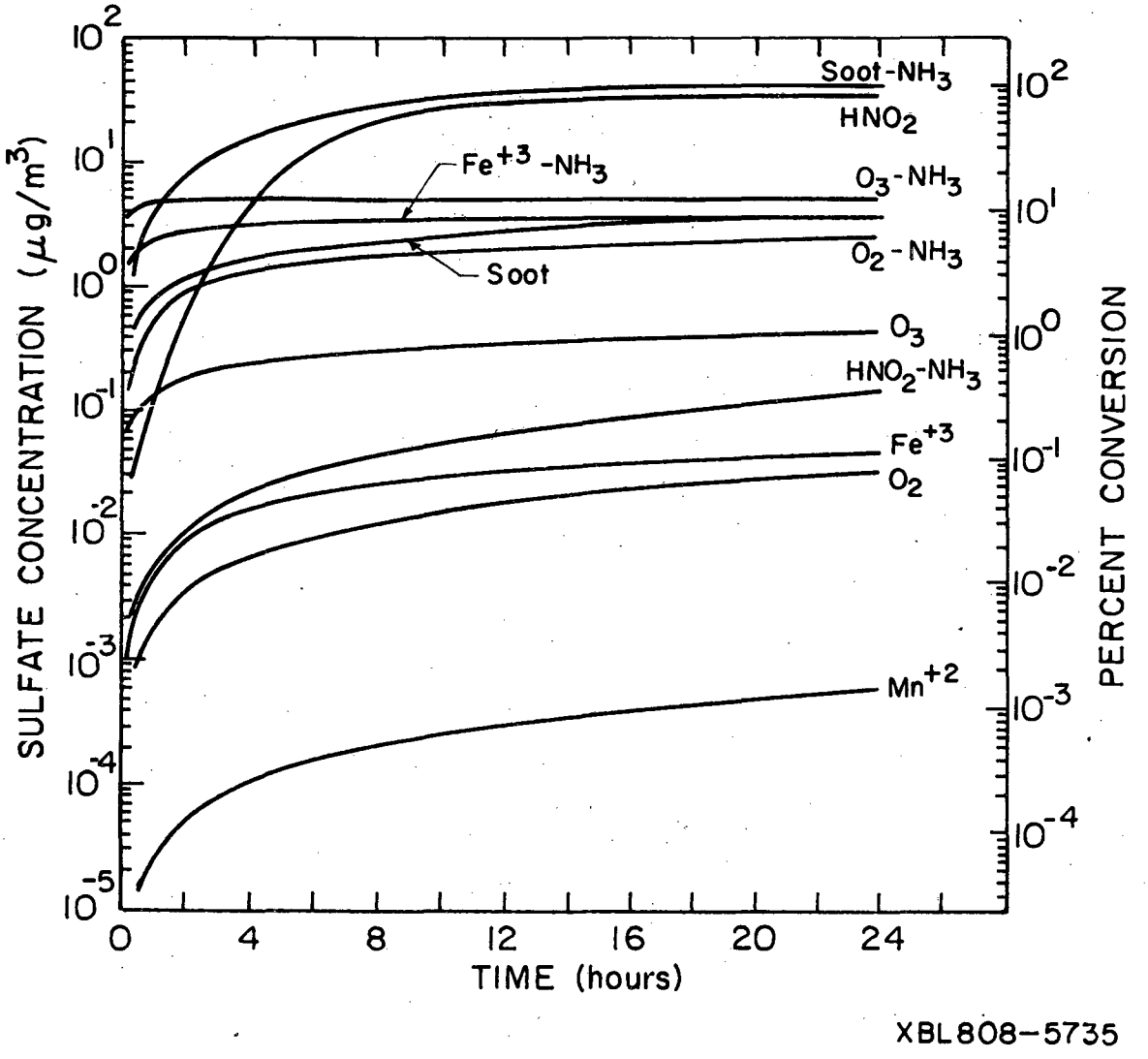

SULFATE CONCENTRATION (μg/m³)
PERCENT CONVERSION
TIME (hours)
Soot-NH3
HNO2
Fe+3 -NH3
O3-NH3
O2-NH3
Soot
O3
HNO2-NH3
Fe+3
O2
Mn+2
XBL808-5735

Figure 5

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