LBL-19398
c.2

Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

RECEIVED
LAWRENCE
BERKELEY LABORATORY

MAY 16 1985

LIBRARY AND
DOCUMENTS SECTION

APPLIED SCIENCE DIVISION

Presented at the Spring 1985 National Meeting of the AIChE, Houston, TX, March 24-28, 1985

KINETICS OF COMBINED SO_2/NO IN FLUE GAS CLEAN-UP

S.G. Chang and D. Littlejohn

March 1985

TWO-WEEK LOAN COPY
This is a Library Circulating Copy which may be borrowed for two weeks.

APPLIED SCIENCE DIVISION

LBL-19398
c.2

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

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.

Kinetics of Combined SO_2/NO in Flue Gas Clean-Up†

S. G. Chang* and D. Littlejohn

Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Abstract

The kinetics of reactions involving SO_2, NO, and ferrous chelate additives in wet flue gas simultaneous desulfurization and denitrification scrubbers are discussed. The relative importance of these reactions are assessed. The relevance of these reactions to spray dryer processes for combined SO_2/NO flue gas clean-up is addressed.

† This work was supported by the Assistant Secretary for Fossil Energy, U.S. Department of Energy under Contract Number DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, Pensylvania.

Kinetics of Combined SO_2/NO Flue Gas Clean-Up

I. Introduction

Wet flue gas simultaneous desulfurization and denitrification processes have been developed by the Japanese in the 70's and have been shown to be very efficient in SO_2 and NO_x removal[1-3] (more than 85% for NO_x and 95% for SO_2). However, these wet processes have not reached the commercial stage yet because they are uncompetitive economically, according to cost evaluation.[4] These cost evaluations, however, were made based on design and knowledge available at that time. Critiques[4] have indicated that these wet processes are in their early stages of development and with their maturation, they could become competitive in cost.

The most promising type of wet process developed so far is based on the addition of ferrous chelates in scrubbing liquor to enhance the absorption of NO by forming nitrosyl ferrous chelates in aqueous solutions. Nitrosyl ferrous chelate can then react[5,6] with dissolved SO_2 to produce N_2, N_2O, dithionate, sulfate and various N-S compounds, while some ferrous chelates are oxidized to ferric chelates, which are inactive. Therefore, this type of process requires regeneration of scrubbing liquors by removing dithionate, sulfate, and N-S compounds from the solutions and reduction of ferric chelate back to ferrous chelates. The chemistry of this type of process is complicated and has not been well investigated. Therefore, an optimum design of a system of this type cannot be achieved. This paper addresses important kinetic information, including those of recent study, involved in this type of process.

II. Kinetics and Mechanisms

(1) Dissolution of NO in aqueous solutions

Nitric oxide can exist in two different forms, dissolved and hydrated, represented respectively by NO (dissolved) and $NO(H_2O)_x$, after dissolution in aqueous solutions.[7] The rate of formation of NO (dissolved) is presumably controlled by mass transfer rate.

The $NO(H_2O)_x$ is formed by a reversible hydrolytic reaction:

$$NO\ (\text{dissolved}) \quad = \quad NO(H_2O)_x \qquad 1$$

The rate constant of this reaction has been determined at 0°, 25°, and 50 °C to be 0.136, 0.141, and 0.15 sec^{-1} respectively. The activation parameters corresponding to these data are $\Delta H^{\neq} = \sim 0$ and $\Delta S^{\neq} = -63$ cal deg^{-1} mol^{-1} referred to 1 M aqueous NO.

Nitric oxide is nonreactive in water (in the absence of oxygen), and the solubility of NO, including both NO (dissolved) and $NO(H_2O)_x$, in aqueous solutions is very small. The solubility coefficient is 1.93×10^{-3} mol/($l$atm) at 25 °C and zero ionic strength.[8] The solubility decreases with increasing temperature; the enthalpy of solution is $\Delta H^{\circ} = -2.94$ kcal/mol. The solubility of NO decreases with increasing ionic strength (μ); this decrease amounts to approximately 8% for $\mu = 0.1$ mol/l. The solubility of NO in aqueous solution was found to be independent of pH over the range 2-13. For 1000 ppm of NO in equilibrium with aqueous scrubbing solution at 50 °C and $\mu = 0.1$ mol/l, the concentration of NO in the aqueous phase is only 1.2×10^{-6} mol/l.

(2) Reversible Reaction of NO with Ferrous Chelates

The binding of NO to $Fe^{2+}(L)$ can be expressed by the following equation:

$$NO\ (\text{dissolved}) + Fe^{2+}(L) \quad \rightleftharpoons \quad Fe^{2+}(L)(NO) \qquad 2$$

where L represents chelates. With the temperature-jump technique, Littlejohn and Chang[9] directly measured the formation and dissociation rate constants of $Fe^{2+}(H_2O)_5(NO)$, $Fe^{2+}(\text{citrate})(NO)$, $Fe^{2+}(acac)_2(NO)$, $Fe^{2+}(EDTA)(NO)$, and $Fe^{2+}(NTA)(NO)$ (Table 1). The temperature-jump apparatus (Figure 1) employed is similar to that described by Czerlinski and Eigen.[10] The source of the energy for the temperature-jump is a high-voltage dc power supply connected to a capacitor through a solenoid switch. After the capacitor is charged, the switch is disconnected. When a variable spark gap is closed, the energy stored in the capacitor can be discharged through a cell containing the reaction under study. A temperature jump of about 8 °C

was created by discharging a 0.25-mF capacitor, charged to 20 kV, through platinum-coated electrodes in the cell, whose volume is approximately 1.4 cm^3. The discharge time is dependent on the ionic strength of the solution but in general less than 10 μs. The temperature jump induces a change in the concentrations of reactants and products as the reaction shifts to a new equilibrium. The shift is monitored by a photomultiplier tube and displayed on an oscilloscope.

The reciprocal of the relaxation time equals the forward rate constant times the sum of the final equilibrium concentration of Fe^{2+}(L) and NO plus the reverse rate constant.[10] When the reciprocal of the relaxation time is plotted against the final concentrations of Fe^{2+}(L) plus NO, the slope of the curve gives the forward rate constant (k_2) and the point of interception gives the reverse rate constant (k_{-2}).

The result of $Fe^{2+}(H_2O)_5(NO)$ is in good agreement with that determined by Kastin *et al.*[11] using the same experimental technique. For both Fe^{2+}(EDTA)(NO) and Fe^{2+}(NTA)(NO), the relaxation times due to the temperature jump were too fast to be measured. However, an upper limit of 10 μs was established for the relaxation times for both complexes. By use of this value with the equilibrium constants determined for Fe^{2+}(EDTA)(NO)[12] and Fe^{2+}(NTA)(NO)[13], the lower limits of formation rate constants were calculated to be 7 x 10^7 and 6 x 10^7 l/mole-sec, respectively; while the lower limits of dissociation rate constants were 35 and 6 sec^{-1}, respectively at 25 °C. Teramoto *et al.*[14] has carried out an experiment using a stirred vessel with a free flat gas-liquid interface and a bubble column, and obtained a formation rate for Fe^{2+}(EDTA)(NO) of 2.6 x 10^8 l/mol-sec at 35 °C, which is consistent with that determined by the temperature-jump technique. From the results listed in Table 1, we can conclude that the formation rate of Fe^{2+}(EDTA)(NO) is at least 85 times faster than that of $Fe^{2+}(H_2O)_5(NO)$; whereas, the dissociation rate of Fe^{2+}(EDTA)(NO) is about 250 times slower than that of $Fe^{2+}(H_2O)_5(NO)$ at 25 °C.

The absorption of NO is enhanced by the presence of ferrous chelate compounds. By using the equilibrium constant of Fe^{2+}(NTA)(NO), for an aqueous scrubbing solution initially containing 0.1 mol/l Fe^{2+}(NTA) at 50 °C, μ = 0.1 mol/L, the fraction of the iron

chelate that is converted to Fe^{2+}(NTA)(NO) is about 36% when the solution is in equilibrium with a gas containing 1000 ppm of NO at 1 atm. For a gas containing 100 ppm of NO the conversion is about 5%. Thus, the presence of the iron chelate increases the capacity of the scrubbing solution for NO by a factor of 30,000 or more.

(3) Reaction of NO with Silfite and Bisulfite

We have recently studied[15] the reactions of NO + $SO_3^{=}$ and NO + HSO_3^{-} using rapid-mixing continuous-flow and stopped-flow techniques in conjuction with UV spectrophotometry for detection of the reaction's product, N-nitrosohydroxylamine-N-sulfonate (NHAS). The extinction coefficient for NHAS was obtained by completley converting a sulfite solution at pH 11 to NHAS by the addition of nitric oxide. The conversion of sulfite to NHAS was confirmed using ion chromatography. The absorbance of the solution was recorded from 200 to 400 nm and these values were converted into extinction coefficients (Figure 2).

The flows of the reactants were varied to produce a range of reactant concentration ratios and range of times between mixing and monitoring. The flow rates ranged from 20 to 500 ml/min. In continuous-flow experiments, the UV spectrum was recorded over a range of 200 to 400 nm, along with the pH of the reacting solution. In stopped-flow experiments, the spectrometer was set at a wavelength where NHAS absorbs (Figure 2). Wavelengths used for monitoring were in the range of 257 to 295 nm, where no other species in the solution absorbed. A recording of the absorption was started and then the flow was stopped abruptly. The record of the absorption vs time was used in rate constant determinations.

A plot of the log of the rate constant vs pH is shown in Figure 3 along with the log percent of sulfite and bisulfite vs pH. If only sulfite reacted with nitric oxide, the data would be expected to match the shape of the sulfite curve. From the data we get the rate expression:

$$\frac{d[NHAS]}{dt} = k_a[NO][HSO_3^-] + k_{a'}[NO][SO_3^=] \qquad \text{(a)}$$

By assuming all of the NO is in hydrated form, we obtain $k_a = 32 \pm 10\ M^{-1}\ sec^{-1}$ and $k_{a'} = 620 \pm 100\ M^{-1}\ sec^{-1}$. The curve for this rate expression is shown in Figure 3 also. The rate constant for the reaction with sulfite ion is much larger than that obtained by Nunes and Powell,[16] who studied the reaction using a stirred reactor by bubbling NO gas into a sulfite solution and obtained an expression:

$$-\frac{d[NO]}{dt} = .132[NO] + .45[NO][SO_3^{=}] \qquad \text{(b)}$$

in M sec^{-1} at 25 °C and pH 13 to 14. They attribute the first term to the hydration of nitric oxide and the second term to the reaction of dissolved nitric oxide with sulfite ion.

NO (dissolved)	→	$NO(H_2O)_x$	1
$NO(H_2O)_x + SO_3^{=}$	→	$^{-}ONSO_3^{-}$	3
NO (dissolved) + $SO_3^{=}$	→	$^{-}ONSO_3^{-}$	4

The reaction of hydrated nitric oxide with sulfite ion was assumed to be much faster than the reaction of dissolved nitric oxide with sulfite ion. The $^{-}ONSO_3^{-}$ intermediate was believed to react rapidly with a second molecule of nitric oxide to form NHAS. They made no mention of whether the second nitric oxide needed to be hydrated or not. Presumably, because of the rapidity by which the intermediate reacts with nitric oxide, the nitric oxide could be either in the dissolved or hydrated form. If this were not the case, the rate expression would be more complex.

In our system, the hydrated form of nitric oxide is formed prior to mixing, so the sulfite-independent term would not be observed and the rate constant we obtain is for the reaction of hydrated nitric oxide with sulfite ion. The rate of the reaction of dissolved nitric oxide with sulfite ion is sufficiently slow that it would not contribute significantly to the formation of NHAS in the time scales in which we observed the reaction. In experiments where the original sulfite ion concentration was in excess of that of nitric oxide, we observed concentrations of NHAS equal to half the original nitric oxide concentration shortly after mixing. This indicated that at least half of the nitric

oxide was in the hydrated form. Otherwise, the NHAS concentration would be lower because the dissolved nitric oxide could not generate NHAS quickly. Other than measurements such as these, we have no indication of what the equilibrium constant is for the process:

$$NO(\text{dissolved}) = NO(\text{hydrated})$$

In the analysis of experimental data and calculating rate constants, it was necessary to correct the results for the hydrolysis of NHAS whose kinetics follow.

(4) Hydrolysis of N-nitrosohydroxylamine-N-sulfonate

NHAS hydrolyzes to produce nitrous oxide and sulfate:

$$^{-}ON(NO)SO_3^{-} \rightarrow N_2O + SO_4^{2-} \qquad 5$$

The rate of this hydrolysis was studied by Seel and Winker[17] and Ackermann and Powell.[18] These authors found that hydrolysis is catalyzed by acid as well as heavy metal ions. By the addition of EDTA in the system it was possible to avoid the catalysis due to heavy metal ions. Seel and Winker have obtained a hydrolysis rate equation:

$$-\frac{d[NHAS]}{dt} = k_5[H^+][NHAS] \qquad \text{(c)}$$

with $k_5 = 1.1 \times 10^4$ sec^{-1}. The rate obtained by Ackermann and Powell without EDTA has a hydrogen ion dependence that is less than first order, and can be expressed as:

$$\frac{d[NHAS]}{dt} = k'_5[H^+]^{0.86}[NHAS]$$

where $k'_5 = 1.6 \times 10^3$ sec^{-1}. The primary effect of trace heavy metal ions appears to be an increase of the decomposition rate at neutral and alkaline pH conditions. The hydrolysis rate constants obtained by Ackermann and Powell[18] and Ackermann[19] were used for the corrections.

(5) Reaction of Ferrous Nitrosyl Chelates with SO_3^{2-}/HSO_3^-

The reaction is known to produce a large number of products,[5,6] including N_2O, N_2, hydroxylamine disulfonate (HADS), SO_4^{2-}, $S_2O_6^{2-}$, and Fe^{3+}. Reports of the reaction have indicated that it is complicated. There are contradictions in the literature as to what the reaction products are, as well as the kinetic behavior.

Sada and co-workers[20] studied this reaction using a system where NO gas was continuously flowed into a Fe^{2+}(EDTA) + Na_2SO_3 solution. They conclude that the reaction proceeds by S(IV) reacting with NO coordinated to the ferrous complex to produce N_2O and Fe^{3+}. Their basis for this conclusion is the appearance of higher concentration of N_2O in solutions of Na_2SO_3 and Fe^{2+}(EDTA) than in solutions of Na_2SO_3 alone when nitric oxide was bubbled through. They attribute NHAS to be the source of N_2O. No rate was given for the reactions of Fe^{2+}(EDTA)(NO) with either SO_3^{2-} or HSO_3^-.

In our study of the reaction,[6] degassed solutions of reagent grade sodium sulfite and/or sodium metabisulfite were added to the spectrophotometer cell and the cell was evacuated. The solution containing the ferrous nitrosyl complex, which was prepared on a vacuum line, was added and the solutions were mixed and placed in the spectrophotometer for monitoring. The absorption spectra of the complex are shown in Figure 4. The initial disappearance of the ferrous nitrosyl chelates could be described as:

$$-\frac{d[Fe^{2+}(L)NO]}{dt} = k[HSO_3^-] + k[SO_3^=][Fe^{2+}(L)NO] \qquad \text{(d)}$$

For L = NTA at 25 °C and pH 3 to 8, $k_1 = 1.2 \times 10^{-5}$ sec^{-1} and $k_2 = 0.13$ M^{-1} sec^{-1} for 10^{-4} M < [Fe(II)(NTA)NO] < 10^{-3} M and 10^{-2} M < [S(IV)] < 10^{-1} M. For L = EDTA at 25 °C and pH 4 to 8, $k_1 = 5.6 \times 10^{-5}$ sec^{-1} and $k_2 = 0.175$ M^{-1} sec^{-1}. For EDTA at 55 °C and pH 4 to 8, $k_1 = 9.0 \times 10^{-5}$ sec^{-1} and $k_2 = 0.60$ M^{-1} sec^{-1}. These values for EDTA are valid for 10^{-4} M < [Fe(II)(EDTA)NO] < 10^{-3} M and 10^{-3} M < [S(IV)] < 10^{-1} M.

In order to understand the reaction mechanisms, we have analyzed reaction products vs reaction time. Gaseous products were analyzed by an Aerograph A700 gas chromatograph with a Porapak Q column. SF_6 was used over most solutions to allow determination of N_2 generated by the reaction mixtures. Occasionally, gas samples

were withdrawn and run on an A.E.I. MS12 mass spectrometer to check the results obtained by gas chromatography.

Ferrous ion concentrations were determined by the 1,10 phenanthroline method. Test solutions were acidified to pH ~ 2.5 to avoid interference from the ligands used in the reaction mixtures.

We have developed a laser Raman spectroscopic[21] and ion chromatographic techniques[22] that can be successfully used in the determinations of N-S compounds in reaction mixtures. Both techniques require only a small amount of the sample and allow simple, rapid and simultaneous determination of these compounds. Figure 5 shows Raman spectra of the N-S compounds along with the sulfate ion reference peak at 980 cm^{-1}. The spectra can be quantified by adding a known amount of a reference compound, such as ClO_4^-, to the sample and comparing peak heights. The peak heights must be corrected for the relative scattering efficiencies of the compounds (Table 2). Using a Dionex 2010i Ion Chromatograph with a conductivity detector, we can make determinations of N-S compounds.

The mechanism we developed for the reaction of Fe(II)(L)NO with sulfite ion is as follows:

$Fe(II)(L)NO$	$=$	$Fe(II)(L) + NO$	2
$NO + SO_3^=$	$\rightarrow$	$(ONSO_3)^=$	4
$NO + xH_2O$	$=$	$NO(H_2O)_x$	1
$NO(H_2O)_x + SO_3^=$	$\rightarrow$	$(ONSO_3)^=$	3
$NO + (ONSO_3)^=$	$\rightarrow$	$^-ON(NO)SO_3^-$	6
$^-ON(NO)SO_3^-$	$\rightarrow$	$N_2O + SO_4^=$	5
$2Fe(II) + (NO)_2SO_3^=$	$\rightarrow$	$2Fe(III) + N_2O + SO_3^=$	7

We did not include a direct reaction between Fe(II)(L)NO and $SO_3^=$ because it appears that the reactions listed account for disappearance of Fe(II)(L)NO when mixed with $SO_3^=$.

While there is uncertainty in k_2 and k_{-2} for Fe(II)(NTA)NO and Fe(II)(EDTA)NO, the rate constants for reaction 2, Littlejohn and Chang,[9] and Teramoto, *et al.*[14] indicate that k_{-1} is on the order of 10^7 M^{-1} sec^{-1}. The equilibrium constants $K_{eq} = \frac{k_2}{k_{-2}}$ are fairly well established[12,13] as being about 10^6 M^{-1} at 25 °C, indicating that k_{-2} is about 10 sec^{-1}. From this approximate value of k_{-2} and the rate equation for NO + $SO_3^=$, we can calculate a rate for Fe(II)(L)NO. However, the calculated rate is considerably faster than that of the observed rate. The calculated rate was obtained assuming that the nitric oxide release by the ferrous chelate reacts at the rate for hydrated nitric oxide.

A more likely assumption would be that the nitric oxide is not hydrated until it is released by the ferrous chelate. Since the hydration rate is so slow[7] ($k \cong 0.14$ at 25 °C), the rate of reaction of Fe(II)(L)NO + $SO_3^=$ no longer depends on k_{-2}, but on K_{eq} and the hydration rate constant. Using this methodology, the calculated rates agree well with the observed rates for both Fe(II)(EDTA)NO and Fe(II)(NTA)NO. For example, with initial concentrations of [Fe(II)(NTA)NO] = 1×10^{-3} M and [$SO_3^=$] = 1×10^{-2} M, the observed rate is 1.3×10^{-6} M sec^{-1}. Using $K_{eq} = 2.0 \times 10^6$ M^{-1}, the calculated rate is 1.4×10^{-6} M sec^{-1}. The calculated rate for Fe(II)(EDTA)NO is slightly larger, in agreement with what is observed.

Measurements of the absorption of nitric oxide by Fe(II)(EDTA) solutions done by Teramoto *et al.*[14] allowed them to estimate k_2 to be on the order of 10^8 M^{-1} sec^{-1} for the EDTA complex. This indicates that NO does not need to become hydrated to bind to the ferrous chelate. This explains why Sada *et al.*[20] saw much more N_2O from the Fe(II)(EDTA) + $SO_3^=$ solutions than from solutions of $SO_3^=$ alone. In the limited time available to extract NO from a gas bubble, the solution with Fe(II)(EDTA) could collect much more because of the relative rates of Fe(II)(EDTA) + NO and $SO_3^=$ + NO (dissolved). This led to their erroneous conclusion that the sulfite ion reacted with coordinated nitric oxide.

At lower pH conditions, where HSO_3^- is the predominant S(IV) species, somewhat different chemistry occurs in the reaction between Fe(II)(L)NO + S(IV). The rate is slower and this can be attributed to the slower rate of NO + HSO_3^- relative to NO + $SO_3^=$.

HADS and $S_2O_6^{=}$ are produced in significant amounts, although N_2O is also present. $S_2O_6^{=}$ is produced by the reaction of Fe(II) with HSO_3^-. This does not occur at high pH conditions where HSO_3^- is not present.

The process by which HADS is produced appears to be somewhat more complicated. At present, the most plausible mechanism based on our experimental data obtained so far is:

$$Fe^{2+}(L)NO + HSO_3^- \quad = \quad Fe^{2+}(L)NOHSO_3^- \qquad 8$$

$$2Fe^{2+}(L)NOHSO_3 \quad \rightarrow \quad 2Fe^{2+}(L) + HON(SO_3^-)_2 + HNO \qquad 9$$

$$Fe^{2+}(L)NOHSO_3^- + Fe^{2+}(L)NO \quad \rightarrow \quad 2Fe^{2+}(L) + NOSO_3^- + HNO \qquad 10$$

$$HSO_3^- + NOSO_3^- \quad \rightarrow \quad HON(SO_3^-)_2 \qquad 11$$

The last step of the process is the same as that proposed[23,24] for the preparation of HADS from bisulfite ion and nitrous acid. The nitroxyl ion, NO^-, could dimerize and decompose to N_2O. Another possible route for HADS formation is by a reaction of $Fe^{2+}(L)$ and NHAS. More work is required to clarify the HADS formation process.

(6) Formation of Nitrogen-Sulfur Compounds

Once HADS is formed, it can further react to form other nitrogen-sulfur compounds (Figure 6). Chang *et al.*[3] has published an extensive review article on the kinetics and mechanisms of important reactions involved.

HADS can hydrolyze to produce hydroxylamine monosulfonate (HAMS) and sulfate

$$HON(SO_3)_2^{2-} + H_2O \xrightarrow{H^+} HONHSO_3^- + HSO_4^- \qquad 12$$

The rate and mechanism of this hydrolysis was performed by Naiditch and Yost.[25]

HAMS hydrolyzes in acidic solution, but at a much slower rate than that of HADS.[25] The hydrolysis of HAMS produces hydroxylamine (HA) and sulfates:

$$HONHSO_3^- + H_2O \xrightarrow{H^+} NH_3OH^+ + HSO_4^- \qquad 13$$

HADS and HAMS can undergo sulfonation to form aminesulfonates.

$$HON(SO_3)_2^{2-} + HSO_3^- \rightarrow N(SO_3)_3^{3-} + H_2O \qquad 14$$

$$HON(SO_3)_2^{2-} + HSO_3^- \rightarrow NH(SO_3)_2^{2-} + HSO_4^- \qquad 15$$

$$HONHSO_3^- + HSO_3^- \rightarrow NH(SO_3)_2^{2-} + H_2O \qquad 16$$

$$HONHSO_3^- + HSO_3^- \rightarrow NH_2SO_3^- + HSO_4^- \qquad 17$$

The rate and mechanisms of these sulfonation reactions were studied by Seel *et al.*[26]

Sulfonation of HA produces sulfamic acid and ammonium bisulfate. The reaction mechanism involves coordination between NH_2OH and SO_2 molecules with subsequent rearrangement to yield products.[27]

$$NH_2OH + SO_2\ H_2O \rightarrow NH_2HSO_3 + H_2O \qquad 18$$

$$NH_2OH + SO_2\ H_2O \rightarrow NH_4HSO_4 \qquad 19$$

Fraser[28] and Gomiscek *et al.*[29] studied the kinetics of this reaction as a function of temperatures and obtained rate constants and enthalpy and entropy of activation.

Aminetrisulfonate (ATS) hydrolyzes[30] rapidly to form aminedisulfonate (ADS) which can undergo further hydrolysis[31] to produce sulfamate.

$$N(SO_3)_3^{3-} + H_2O \xrightarrow{H^+} NH(SO_3)_2^{2-} + HSO_4^- \qquad 20$$

$$HN(SO_3)_2^{2-} + H_2O \xrightarrow{H^+} H_2NSO_3^- + HSO_4^- \qquad 21$$

(7) Oxidation of Ferrous Chelates to Ferric Chelates

Flue gas contains about 5% oxygen. When dissolved, oxygen can oxidize ferrous ions to ferric ions which are inactive for coordination with NO. The oxidation rate of

ferrous ions is accelerated in the presence of chelating agents, EDTA and NTA. This acceleration may be ascribed to the stabilization of the oxidized form by the chelation.

Kurimura *et al.*[32] studied the oxidation of Fe^{2+}(EDTA) and Fe^{2+}(NTA) by dissolved oxygen in aqueous solutions and suggested that the oxidation proceeds through two parallel reaction paths, one of which involves the oxidation of the protonated chelate while the other involves the oxidation of the normal chelate. The reaction mechanisms suggested[32,33] are as follows:

$Fe^{2+}(HL) + O_2$	k_{22}	$Fe^{3+}(L) + HO_2^-$	22
$Fe^{2+}(L) + O_2$	k_{23}	$Fe^{3+}(L) + O_2^-$	23
$O_2^- + H^+$	$\rightarrow$	HO_2	24
$Fe(II) + HO_2$	$\rightarrow$	$Fe(III) + HO_2^-$	25
$HO_2^- + H^+$	$=$	H_2O_2	26
$Fe(II) + H_2O_2$	$\rightarrow$	$Fe(III) + OH^- + OH$	27
$Fe(II) + OH$	$\rightarrow$	$Fe(III) + OH^-$	28

In these equations, Fe(II) and Fe(III) represent the ferrous and ferric ion species respectively. The rate equation for the oxidation is:

$$\frac{d[Fe^{3+}]}{dt} = 4k_{22}[Fe^{2+}(HL)][O_2] + 4k_{23}[Fe^{2+}(L)][O_2] \qquad \text{(e)}$$

For EDTA, $k_{22} = 6.8 \times 10^3$ and $k_{23} = 2.7 \times 10^2\ M^{-1}\ sec^{-1}$; while for NTA, $k_{23} = 80\ M^{-1}\ sec^{-1}$ at 25 °C. As can be seen from these results, protonated chelates proceed more rapidly than that of the normal chelate.

In addition to the oxidation by O_2, Fe^{2+}(L) can be converted to Fe^{3+}(L) in an aqueous system containing only Fe^{2+}(L) + NO + SO_3^{2-}, without the presence of oxygen[6] (Figure 7). Preliminary results from our laboratory, by mixing Fe^{2+}(NTA) or Fe^{2+}(EDTA) with NHAS have shown the formation of Fe^{3+} and the liberation of N_2O. An oxidation-reduction reaction such as:

$$2H^+ + 2Fe(II) + NHAS \rightarrow 2Fe(III) + N_2O + SO_3^= + H_2O \qquad 29$$

may occur. It would be helpful to have a rate expression to predict the amount of oxidation of Fe(II) in the presence of NHAS. By making several assumptions, a tentative rate expression can be obtained for measurements of the appearance of Fe(III) in mixtures of Fe(II)(NTA)NO and $SO_3^=$. First, we assume that the reaction has first order dependence on both Fe(II) and NHAS:

$$\frac{d[Fe(III)]}{dt} = k[NHAS][Fe(II)] \qquad \text{(f)}$$

Then, by assuming that all the NO from Fe(II)(NTA)NO reacts to form NHAS and all the N_2O evolved comes from NHAS, we can obtain an estimate of the NHAS concentration with time. From this, a value of $k \sim 0.3\ M^{-1}\ sec^{-1}$ is obtained for Fe(II)(NTA). The rate may be different for different chelates and there may be some pH dependence also. Further work is needed to obtain a better understanding of this reaction.

To compare the relative rates of oxidation of Fe(II) by oxygen and NHAS, we can consider a typical scrubber situation where there is 5% O_2, 750 ppm NO and 0.01 M Fe(II)(NTA) in the scrubbing solution. From the conditions listed, using a Henry's constant for O_2 of 2.5×10^{-4} M atm^{-1}, the oxidation of Fe(II) by O_2 can be calculated:

$$\frac{d[Fe(III)]}{dt} = 4.0 \times 10^{-5} M\ sec^{-1}$$

To find the rate of oxidation due to NHAS, a value is needed for the NHAS concentration. The NO concentration in solution is 1.4×10^{-6} M when it is in equilibrium with the NO in the gas phase. The reaction between hydrated NO and $SO_3^=$ is the most important formation mechanism for NHAS. We can assume that the rate of hydration of NO is close to the rate of formation of NHAS:

$$\frac{d[NHAS]}{dt} = \frac{d[NO(H_2O)_x]}{dt} = k_1(NO) \qquad \text{(g)}$$

Similarly, the rate of destruction of NHAS will occur primarily by the reaction with

Fe(II) under alkaline conditions, where the hydrolysis rate is slow.

$$\frac{-d[NHAS]}{dt} = \frac{1}{2}\frac{d[Fe(III)]}{dt} = \frac{1}{2}k_{29}[Fe(II)][NHAS] \qquad \text{(h)}$$

If the NHAS concentration changes slowly with time, the steady state approximation can be used to estimate its concentration:

$$\frac{d[NHAS]}{dt} \approx 0 = k_1[NO] - \frac{k_{29}}{2}[NHAS][Fe^{II}(NTA)] \qquad \text{(i)}$$

$$[NHAS] = \frac{2k_1}{k_{29}}\frac{[NO]}{[Fe^{II}(NTA)]} \qquad \text{(j)}$$

For the above conditions, the NHAS concentration is about 1.3×10^{-4} M. Inserting this into the equation for Fe(III) formation by NHAS, one obtains d[Fe(III)]/dt = 4×10^{-7} M sec^{-1}. This value, while somewhat uncertain, is much smaller than the rate of oxidation by dissolved O_2.

(8) Reduction of Ferric Chelates by HSO_3^- and Formation of Dithionate

Fe^{3+}(EDTA) can be reduced by HSO_3^-, while dithionate together with a small amount of SO_4^{2-} are produced.[34] It was found that the rate of reduction of Fe^{3+}(EDTA) is first order with respect to HSO_3^- and Fe^{3+}(EDTA), and inversely first order with respect to Fe^{2+}(EDTA) concentration.

$$\frac{-d[Fe^{3+}(EDTA)]}{dt} = k[Fe^{3+}(EDTA)][HSO_3^-]/[Fe^{2+}(EDTA)] \qquad \text{(k)}$$

The rate constant k is 8.8×10^{-6} sec^{-1} at 55 °C. The apparent activation energy was found to be 21.3 kcal/mol. The following reaction mechanism were suggested:[34]

$Fe^{3+}(EDTA) + HSO_3^-$	=	$FeSO_3^+ + H^+ + EDTA$	30
$FeSO_3^+$	=	$Fe^{2+} + SO_3^-$	31
$Fe^{2+} + EDTA$	=	$Fe^{2+}(EDTA)$	32

$$SO_3^- + H^+ \rightarrow HSO_3^- \qquad 33$$

$$HSO_3 + HSO_3 \rightarrow S_2O_6^{2-} + 2H^+ \qquad 34$$

In a wet scrubber system, where there is 750 ppm NO, 0.01 M HSO_3^- and 0.01 M of Fe^{2+}(EDTA) initially, if we assume at one point after reaction, half of Fe^{2+}(EDTA) in the absorber is oxidized to Fe^{3+}(EDTA) and the remaining half Fe^{2+}(EDTA) is in equilibrium with 750 ppm of NO, then the rate of reduction of Fe^{3+}(EDTA) by HSO_3^- can be calculated to be about 1.76×10^{-7} M sec^{-1} which is much slower than the rate of oxidation of Fe^{2+}(EDTA) by dissolved O_2. However, as the concentration of Fe^{2+}(EDTA) decreases and that of Fe^{3+}(EDTA) increases, the condition for the reduction process improves.

III. Effect of Ferrous Chelate Additives on NO Removal in Spray Dryer Processes.

Using the rate constants obtained for the reaction of NO and SO_3^{2-}/HSO_3^- and NO + Fe^{2+}(L), one can make estimations of the rate of removal of NO from flue gases by scrubbing solutions with and without ferrous chelates. From the kinetic theory of gases,[35,36] the rate of collision of a gas with a surface area A is:

$$R = \frac{n\bar{v}A}{4} \qquad (l)$$

where n is the concentration of gas (molecules/cm^3) and $\bar{v}$ is the mean velocity.

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}} \qquad (m)$$

Here T is absolute temperature (K), k is the Boltzmann constant and m is the molecular weight. If A is the total area of the droplets of scrubbing solution in a unit volume and n is the concentration of either SO_2 or NO, the concentration vs time can be determined by:

$$\frac{dn}{dt} = -\left(\frac{\bar{v}A}{4}\right)n \qquad \text{(n)}$$

Integrating, one obtains $n(t) = n_o e^{\frac{-t}{\tau}}$ (o) where $\tau = \frac{4}{\bar{v}A}$. This assumes that the droplets can absorb an infinite amount of SO_2 or NO.

Using the following spray dryer parameters from PETC,[37] one can do calculations on absorption efficiency for NO.

Volume:	230 cu ft = 2.8×10^4 cm^3
Slurry Composition:	20% CaO (by wt.)
Slurry Flow Rate:	350 lb/hr = 44 g/sec
Flue Gas Flow Rate:	1200 SCF/hr
SO_2 Concentration:	2500 ppm = 6.25×10^{16} molecules/cm^3
NO Concentration:	750 ppm = 1.85×10^{16} molecules/cm^3
Average Initial Droplet Radius:	50 μm
Residence Time:	10 sec

The Henry's constant[8] for NO at 25 °C is 1.93×10^{-3} M/atm and the Henry's constant of SO_2 at 25 °C is 1.24 M/atm. Hydrated SO_2 rapidly converts[38] to HSO_3^- and $SO_3^=$ if the solution is sufficiently basic. The CaO, which converts to $Ca(OH)_2$ on mixing with water acts as a buffer and also limits the concentration of $SO_3^=$ because of the limited solubility of $CaSO_3$ (.0043 g/100 ml H_2O at 18 °C in the form of $CaSO_3$ $2H_2O$).

Using the above information, one can calculate the 7.2×10^7 droplets/sec are formed and there are 2.6×10^4 droplets/cm^3. From this, the rate of absorption of NO and SO_2 can be inferred from equation (o). The results indicate that NO and $SO_3^=$ reach their maximum concentrations in a small fraction of a second, assuming that the interior of the droplet is well-mixed. Consequently, the limiting factor in the removal of NO from the flue gas will be the chemistry occurring within the droplet.

The reactions that will occur when NO and $SO_3^=$ are present in the droplet are:

$$NO\ (dissolved) + SO_3^= \xrightarrow{k_4} {}^-ONSO_3^-; \quad k_4 = 0.45\ M^{-1}\ sec^{-1} \qquad 4$$

$$NO\ (dissolved) + xH_2O \xrightarrow{k_1} NO(H_2O)_x; \quad k_1 = 0.14\ sec^{-1} \qquad 1$$

$$NO(H_2O)_x + SO_3^= \xrightarrow{k_3} {}^-ONSO_3^-; \quad k_3 = 620\ M^{-1}\ sec^{-1} \qquad 3$$

Using $[NO] = 1.9 \times 10^{-3}$ M/atm 7.5×10^{-4} atm $= 1.4 \times 10^{-6}$ M and $[SO_3^=] = 2.5 \times 10^{-4}$ M (from the solubility of $CaSO_3$), the rates for these reactions can be calculated:

$$\text{rate (4)} = k_4[NO][SO_3^=] = 1.6 \times 10^{-10}\ M/sec$$

$$\text{rate (1)} = k_1[NO] = 2.0 \times 10^{-7}\ M/sec$$

$$\text{rate (3)} = k_3[NO(H_2O)_x][SO_3^=] = 0.155\,[NO(H_2O)_x]$$

The rate of the third reaction can be no faster than that of the first reaction and the sum of $[NO_{dis}] + [NO(H_2O)_x] = 1.4 \times 10^{-6}$ M. With this, the rate (3) $= 1.0 \times 10^{-7}$ M/sec and is much faster than the rate of the fourth reaction, which can be ignored. The ${}^-ONSO_3^-$ product will quickly react with a second NO molecule to form NHAS. Assuming the rate is constant for the ten second lifetime of the droplet, the amount of NO removed can be calculated:

$$2 \times 1.0 \times 10^{-7}\ M/sec \times 10\ sec \times 5.2 \times 10^{-10}\ l \times 6.0 \times 10^{23}\ \frac{\text{molecules}}{\text{mole}} = 6.3 \times 10^{8}$$
molecules NO removed per droplet

Converting this to the number of molecules removed per cm^3 of gas, the percent NO removed can be calculated:

$$6.3 \times 10^{8}\ molecules/droplet \times 2.6 \times 10^{4}\ droplets/cm^3 = 1.6 \times 10^{3}\ molecules/cm^3$$

This is about 0.1% of the 1.85×10^{16} molecules/cm^3 of NO initially present.

To improve the absorption of nitric oxide by the droplets, a ferrous chelate complex, such as Fe(II)(EDTA), can be added to slurry. Fe(II)(EDTA) can efficiently bind nitric oxide to form Fe(II)(EDTA)NO. If 0.01 M Fe(II)(EDTA) is added to the slurry for the system with the conditions mentioned above, the amount of nitric oxide the slurry can absorb can be calculated. Immediately after droplet formation, there will be 1.35×10^{-5} l of slurry per cm^3 of gas. For 0.01 M Fe(II)(EDTA), this converts to 8.1×10^{16} molecules of Fe(II)(EDTA) per cm^3, which is greater than the number of NO molecules/cm^3.

To determine the rate of formation of Fe(II)(EDTA)NO in a droplet, both the transport and chemistry need to be considered. From Equation (0), it can be seen that the rate of absorption does not depend on the gas concentration. Again, the nitric oxide in the gas phase should come into eqilibrium with the droplet liquid phase in much less than a second. The formation of Fe(II)(EDTA)NO is reversible:

$$\text{Fe(II)(EDTA)} + \text{NO} \underset{}{\overset{k_2}{\rightleftharpoons}} \text{Fe(II)(EDTA)NO} \qquad 2$$

and does not depend on the hydration of nitric oxide since dissolved nitric oxide readily reacts with Fe(II)(EDTA). The forward rate constant, k_2, is quite fast, on the order of 10^7 M^{-1} sec^{-1}. The reverse rate constant, k_{-2}, can be estimated from $K_{eq}=k_2/k_{-2}$. The equilibrium constant, K_{eq}, is about 1×10^6 M^{-1} at 25 °C, so $k_{-2} \approx 10$ sec^{-1}.

The rate of formation is then equal to k_2[Fe(II)(EDTA)][NO]. Initially the rate would be about 10^{-1} M sec^{-1}, but this will decrease as NO concentration decreases. With this high a rate, most of the Fe(II)(EDTA)NO produced will form in less than a second and the droplet will still be in an environment similar to its initial environment. So the amout of Fe(II)(EDTA)NO initially formed can be estimated from the initial concentration of NO present. Using the equilibrium constant for Fe(II)(EDTA)NO and the Henry's constant for NO, we can calculate that about 80% of the nitric oxide in the gas will be converted into Fe(II)(EDTA)NO. The concentration of Fe(II)(EDTA)NO will be 1.8×10^{-3} M and the concentration of NO in the droplet will be 2.2×10^{-7} M and NO in the gas will be 120 ppm.

However, as the droplet passes through the flue gas, it will heat up. This has the effect of reducing the liquid volume through evaporation and changing the kinetics due

to the temperature dependence of the rate constants and equilibrium constants. The increase in temperature will also reduce the solubility of a number of species, reducing their concentration in solution. If the droplet loses all its water by evaporation, the NO attached to the Fe(II)(EDTA) will dissociate and return to the gas phase. The net result would be little changed from the case of the droplet without Fe(II)(EDTA), since the primary mechanism for loss of NO is the reaction:

$$NO(H_2O)_x + SO_3^{=} \rightarrow {}^{-}ONSO_3^{-} \qquad 3$$

The presence of Fe(II)(EDTA)NO would have little effect on the reaction while the droplet is falling, so that droplets with or without Fe(II)(EDTA)NO would remove about the same amount of NO if they dry out completely.

If some liquid remains in the droplet after it has passed through the flue gas, the presence of Fe(II)(EDTA) is likely to improve the NO removal rate. Once a droplet without Fe(II)(EDTA) was no longer in contact with the flue gas, the NO within it would be quickly depleted by reaction with $SO_3^{=}$. A droplet with Fe(II)(EDTA) would have a larger amount of NO within it, largely in the form of Fe(II)(EDTA)NO. This would also react with $SO_3^{=}$. The degree of increased removal of NO by droplets with Fe(II)(EDTA)NO would depend on a number of factors, including final liquid volume, liquid temperature, pH, and amount of interaction with the flue gas. Without detailed knowledge of these factors, it is difficult to predict the degree of enhancement that Fe(II)(EDTA) would provide for NO removal.

The effects of oxygen have not yet been considered. Oxygen can oxidize sulfite ion to sulfate ion, nitric oxide to nitrogen dioxide, and ferrous ion to ferric ion. Of these, the oxidiation of ferrous ion is likely to have the most significant effect on the absorption of nitric oxide. In a typical scrubber, oxygen concentrations are about 5% and the Henry's constant for oxygen is 2.5×10^{-4} M atm^{-1}, which yields $[O_2] = 1.25 \times 10^{-5}$. With a Fe(II)(EDTA) concentration of 0.01 M, the calculated oxidation rate under the alkaline condition (using Equation (e)) is 1.35×10^{-4} M sec^{-1}. In ten seconds, less than 15% of the Fe(II) will be oxidized. This would also be true for 0.1 M Fe(II)(EDTA).

Acknowledgements

We appreciate the support and encouragement of Michael Perlsweig, Joseph Strakey, and John Williams.

References

1. Yaverbaum, L.H., "Nitrogen Oxides Control and Removal, Recent Developments"; Noyes Data Corp: Park Ridge, NJ, 1979.

2. Martin, A.E., Ed. "Emission Control Technology for Industrial Boilers"; Noyes Data Corp: Park Ridge, NJ 1981.

3. Chang, S.G., Littlejohn, D., Lin, N.H. *ACS Symp. Ser.* 1982, *188, No. 118*, 127-152.

4. Maxwell, J.D., Tarkington, T.W., and Burnett, T.A., "Preliminary Economic Analysis of NO_x Flue Gas Treatment Processes Using TVA and EPRI Economic Premises," EPRI CS-2075 (1981), p. 168.

5. Chang, S.G., Littlejohn, D., and Lynn, S. "Effects of Metal Chelates on Wet Flue Gas Scrubbing Chemistry," Environ. Sci. and Technol. *17*, 649 (1983).

6. Littlejohn, D., and Chang, S.G. "Reaction of Ferrous Nitrosyl Complexes with Sulfite Ion," LBL-17962, submitted to Inorg. Chem. for publication (1984).

7. Nunes, T.L., and Powell, R.E. "The Copper(I)-Catalyzed Reduction of Nitric Oxide by Tin(II) Chloride," Inorg. Chem. *9*, 1913 (1970).

8. Armor, J.N. "Influence of pH and Ionic Strength upon Solubility of NO in Aqueous Solution," J. Chem. Eng. Data *19*, 82 (1974).

9. Littlejohn, D., and Chang, S.G. "Kinetic Study of Ferrous Nitrosyl Complexes," J. Phys. Chem. *86*, 537 (1982).

10. Czerlinski, G., and Eigen, M. "Eine Temperatursprung Methode zur Untersuchung Chemischer Relaxation," Elektrochem., *63*, 652 (1959).

11. Kustin, K., Taub, I.A., and Weinstock, E. "A Kinetic Study of the Formation of the Ferrous-Nitric Oxide Complex," Inorg. Chem., *5*, 1079 (1966).

12. Hishinuma, Y., Kaji, R., Akimoto, H., Nakajima, F., Mori, T., Kamo, T., Arikawa, Y., and Nozawa, S. "Reversible Binding of NO to Fe(II)(EDTA)," Chem. Soc. Jap. Bull. *52*, 2863 (1979).

13. Lin, N., Littlejohn, D., and Chang, S. "Thermodynamics and Kinetics of the Coordination of NO to $Fe^{II}NTA$ in Aqueous Solutions," I & EC Proc. Design & Development, *1*, 725 (1982).

14. Teramoto, M., Hiramine, S., Shimada, Y., Sugimoto, Y., and Teranishi, H. "Absorption of Dilute Nitric Monoxide in Aqueous Solutions of Fe(II)(EDTA) and Mixed Solutions of Fe(II)(EDTA) and Na_2SO_3," J. Chem. Eng. of Japan, *11*, 450 (1978).

15. Littlejohn, D., and Chang, S.G. "Kinetics of the Reaction of Nitric Oxide with Sulfite and Bisulfite," manuscript in preparation for publication.

16. Nunes, T.L., and Powell, R.E. "Kinetics of the Reaction of Nitric Oxide with Sulfite," Inorg. Chem. *9*, 1916 (1970).

17. Seel, F., Winkler, R. "Kinetik des Saurekatalysieten Zerfalls des Nitrosohydroxylaminsulfonat-Ions," Z. Naturforsch, *18a*, 155 (1963).

18. Ackermann, M.N., and Powell, R.E. "Air Oxidation of Hydroxylamine-N-Sulfonate," Inorg. Chem. *6*, 1718 (1967).

19. Ackermann, M.N. "Alkaline Hydrolysis and Oxidation of Hydroxylamine-N-Sulfonate," Ph.D. Thesis University of California, Berkeley (1966).

20. Sada, E., Kumazawa, H., and Takada, Y. "Chemical Reactions Accompanying Absorption of NO into Aqueous Mixed Solutions of Fe^{II}-(EDTA) and Na_2SO_3," I E&C. Fundam. *23*, 60 (1984).

21. Littlejohn, D., and Chang, S.G. "Identification of Species in a Wet Flue Gas Desulfurization and Denitrification System by Laser Raman Spectroscopy," Environ. Sci. & Tech. *18*, 305 (1984).

22. Littlejohn, D., and Chang, S.G. "Chemical Analysis of Hydroxylamine Sulfonates, Amine Sulfonates, and N-nitrosohydroxylamine-N-sulfonate by Ion Chromatography," manuscript in preparation for publication.

23. Oblath, S.B., Markowitz, S.S., Novakov, T. and Chang S.G. "Kinetics of the Initial Reaction of Nitrite Ion in Bisulfite Solutions," J. Phys. Chem. *86*, 4853 (1982).

24. Oblath, S.B., Markowitz, S.S., Novakov, T. and Chang, S.G. "Kinetics of the Formation of Hydroxylamine Disulfonate by Reaction of Nitrite with Sulfite," J. Phys. Chem. *85*, 1017 (1981).

25. Naiditch, S., and Yost, D.M. "The Rate and Mechanism of the Hydrolysis of Hydroxylamine Disulfonate Ion," J. Am. Chem. Soc. *63*, 2123 (1941).

26. Seel, V.F., Degener, E., and Knorre H. "Stochiometrie und Kinetik der Umsetzungen von Hydroxylamin-N-Sulfonaten mit Hydrogensulfit," Z. Anorg. Allg. Chem. *299*, 122 (1959).

27. Brackman, D.S., and Higginson, W.C.E. "The Reaction Between Hydroxylamine and Sodium Sulphite in Solution in Dilute Acid," J. Chem. Soc. London, 3896 (1953).

28. Fraser, R.T.M. "The Hydroxylamine-Sulphur Dioxide Reaction," J. Chem. Soc., London 1747 (1965).

29. Gomiscek, S., Clem. R., Novakov, T., and Chang, S.G. "Kinetics of the Reaction Between Hydroxylamine and Sodium Bisulfite," J. Phys. Chem. *85*, 2567 (1981).

30. Sisler, H.H., and Audrieth, L.F., "The Preparation of Sulfamic Acid by the Hydroxylamine-Sulfur Dioxide Reaction," J. Am. Chem. Soc. *61*, 3389 (1939).

31. Doyle, G.J., and Davidson, N., "The Kinetics of the Acid-Catalyzed Hydrolysis of Amine Disulfonate Ion; The Third Ionization Constant of Amine Disulfonic Acid," J. Am. Chem. Soc. *71*, 3491 (1949).

32. Kurimura, Y., Ochiai, R., and Matsuura, N. "Oxygen Oxidation of Ferrous Ions Induced by Chelation," Chem. Soc. Jap. Bull. *41*, 2234 (1968).

33. Kurimura, Y., and Kuriyama, H. "The Kinetics of the Autoxidation of Ferrous Ions in Aqueous Tripolyphosphate Solutions," Chem. Soc. Jap. Bull. *42*, 2238 (1969).

34. Sato, T., Simizu, T., and Okabe, T. "The Formation of Dithionate by the Reaction of Fe(III)-EDTA with Sodium Sulfite," Nippon Kagakukaishi, 361 (1978).

35. Present, R. "The Kinetic Theory of Gases," McGraw Hill, New York (1958).

36. Benson, S.W., "The Foundations of Chemical Kinetics," McGraw Hill, New York (1960).

37. Private communication with Dr. James T. Yeh of Pittsburgh Energy Technology Center, DOE on March 18, 1985.

Table 1.

Kinetic and Thermodynamic Data for Reversible NO Coordination to Ferrous Chelates

ferrous chelates	k_1, mol/(L·s)	k_{-1}, s^{-1}	K, L/mol at 298 K	ΔH°, kcal/mol	ΔS°, eu
$Fe^{2+}(H_2O)_5(NO)$	$(7.1 \pm 1.0) \times 10^5$	$(1.5 \pm 0.6) \times 10^3$	$(4.7 \pm 2.0) \times 10^2$ [a]		
$Fe^{2+}(acac)_2(NO)$	$(4.0 \pm 3.0) \times 10^2$	24 ± 2	17 ± 14 [c]		
$Fe^{2+}(oxal)(NO)$			$\sim 1.0 \times 10^5$		
$Fe^{2+}(cit)(NO)$			4.9×10^4	-8.6	-7.4
$Fe^{2+}(cit)(OH^-)(NO)$			2.1×10^5	-3.7	12.0
$Fe^{2+}(IDA)(NO)$			2.1×10^5	-9.1	-6.3
$Fe^{2+}(NTA)(NO)$	$\geq 7 \times 10^7$	≥ 35	2.14×10^6 [b]	-11.94 [b]	-11.0 [b]
$Fe^{2+}(EDTA)(NO)$	$\geq 6 \times 10^7$	≥ 6	1.15×10^7 [c]	-15.8 [c]	-20.7 [c]

Table 2. **Raman shifts and relative molar intensities of species studied**

Species	Raman shift (cm^{-1})	Relative molar intensity[a]
NO_2^-	818	0.053
	1240	∿ 0.025
	1331	0.125
NO_3^-	1050	0.95
$N_2O_2^=$	692[b]	weak[b]
	1115[b]	weak[b]
	1383[b]	strong[b]
N_2O	1285	∿ 0.18
$SO_3^=$	967	0.12
HSO_3^-	1023	0.10
$SO_4^=$	∿ 455	∿ 0.07
	981	1.00
$S_2O_5^=$	1055	∿ 0.9
HSO_4^-	1050	0.05
HADS	∿ 700	∿ 0.20
	1084	1.43
HAMS	∿ 420	∿ 0.13
	∿ 760	∿ 0.08
	1058	0.48
HA (pH ≤ 7)	1004	0.21
HA (pH ≥ 9)	918	0.09
ATS	1097	0.10
ADS	1084	0.056
SA (pH ≤ 1)	1063	c
SA (pH ≥ 3)	1049	0.41

[a] $SO_4^=$ 981 cm^{-1} line = 1.000

[b] Rauch, J.E.; Decius, J.C., Spectrochim. Acta 1966, 22, 1963.

[c] No value obtained.

Figure Captions

Figure 1 Temperature-jump apparatus. This setup is used for determining the formation and dissociation rate constants and equilibrium constants for the reversible binding of NO to various metal chelates in aqueous solutions.

Figure 2 Absorption spectrum of N-nitrosohydroxylamine-N-sulfonate from 200 to 350 nm.

Figure 3 A plot of the logarithm of the rate constant of the reaction between NO and S(IV) vs pH along with the logarithm of percent of sulfite and bisulfite vs pH.

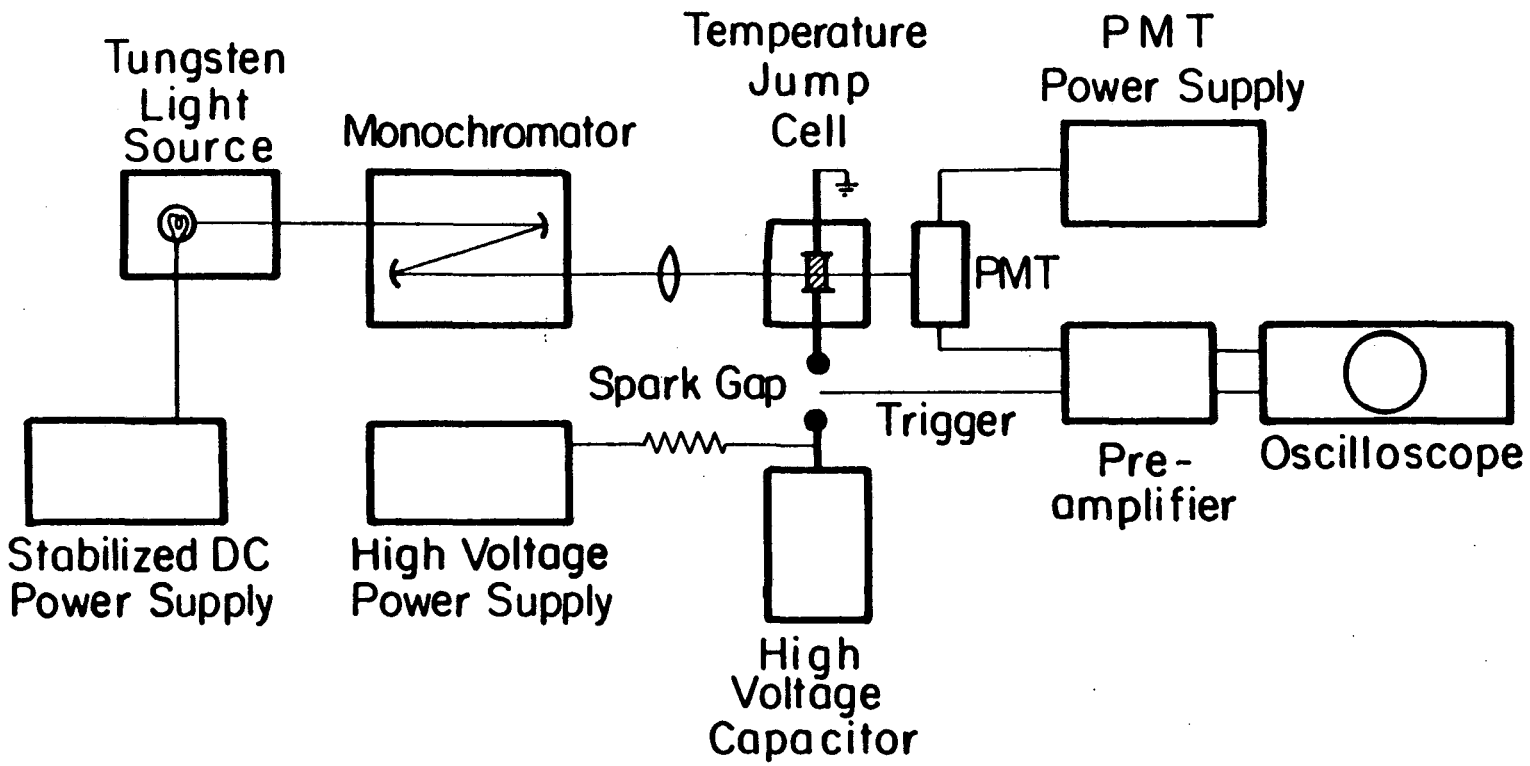
Figure 4 Absorption spectra of ferrous nitrosyl chelates from 800 to 300 nm. The dashed lines represent the absorption spectra of the complexes without NO.

Figure 5 Raman shifts obtained for some nitrogen-sulfur compounds. A sulfate ion peak at 981 cm^{-1} is used as a reference.

Figure 6 Reactions involving nitrogen-sulfur compounds that occur as a result of the reaction between ferrous nitrosyl chelates and sulfite/bisulfite ion in aqueous solutions.

Figure 7. Reactants and product concentrations as a function of time after mixing of Fe^{2+}(NTA)NO with sulfite/bisulfite ions.

Temperature Jump Apparatus



XBL819-6549

Figure 1

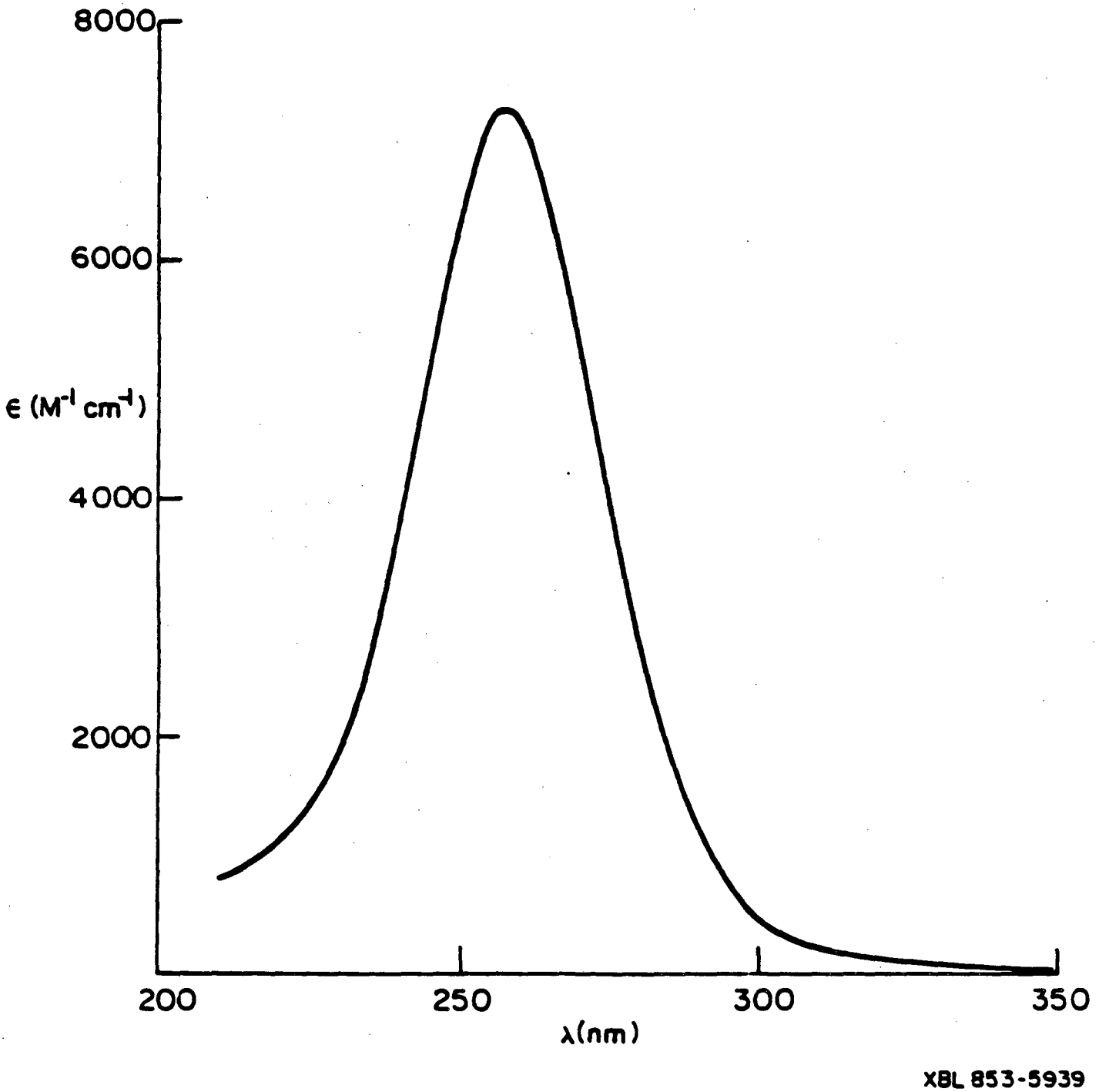


Figure 2

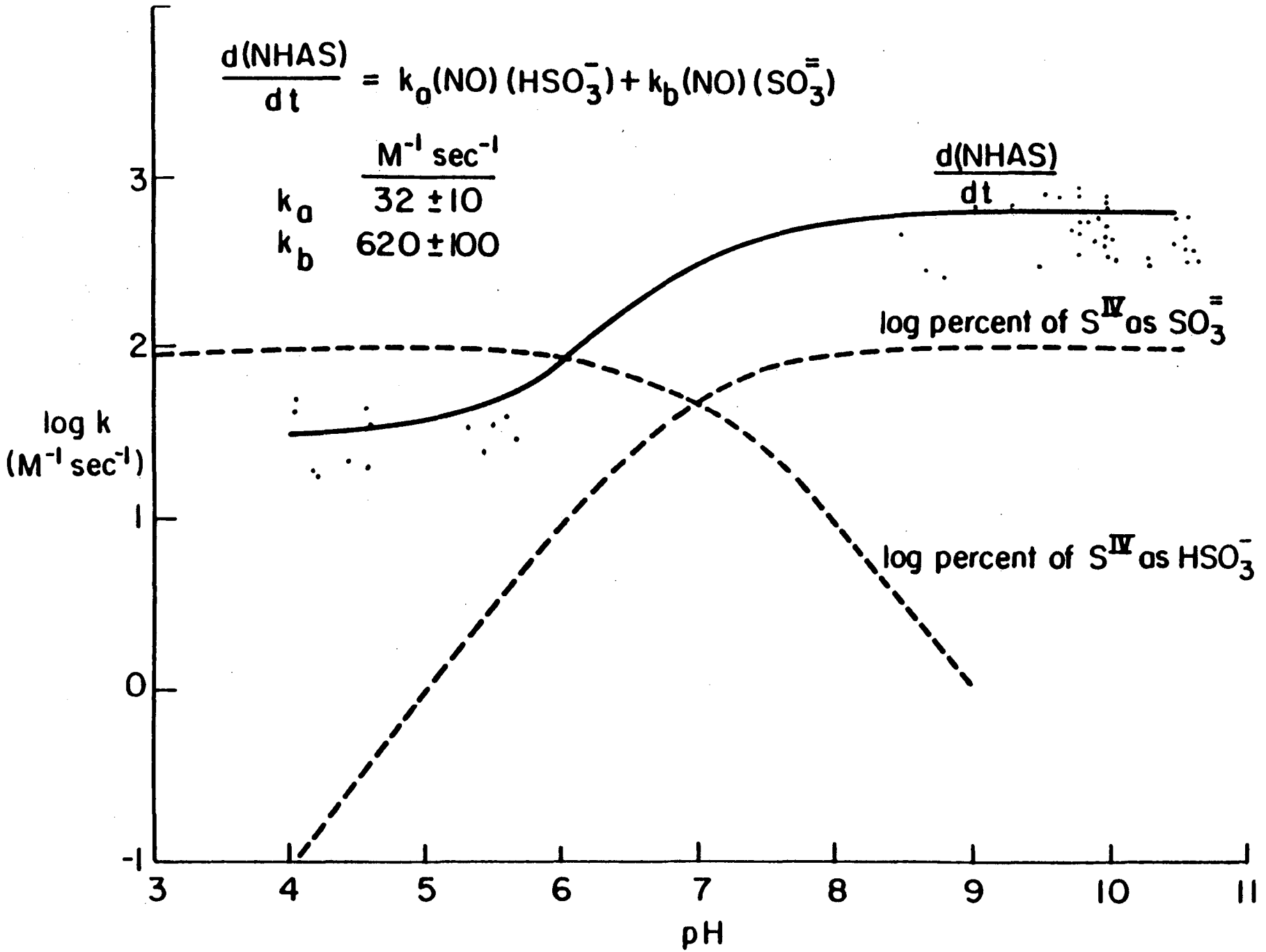


Figure 3

XBL853-5938

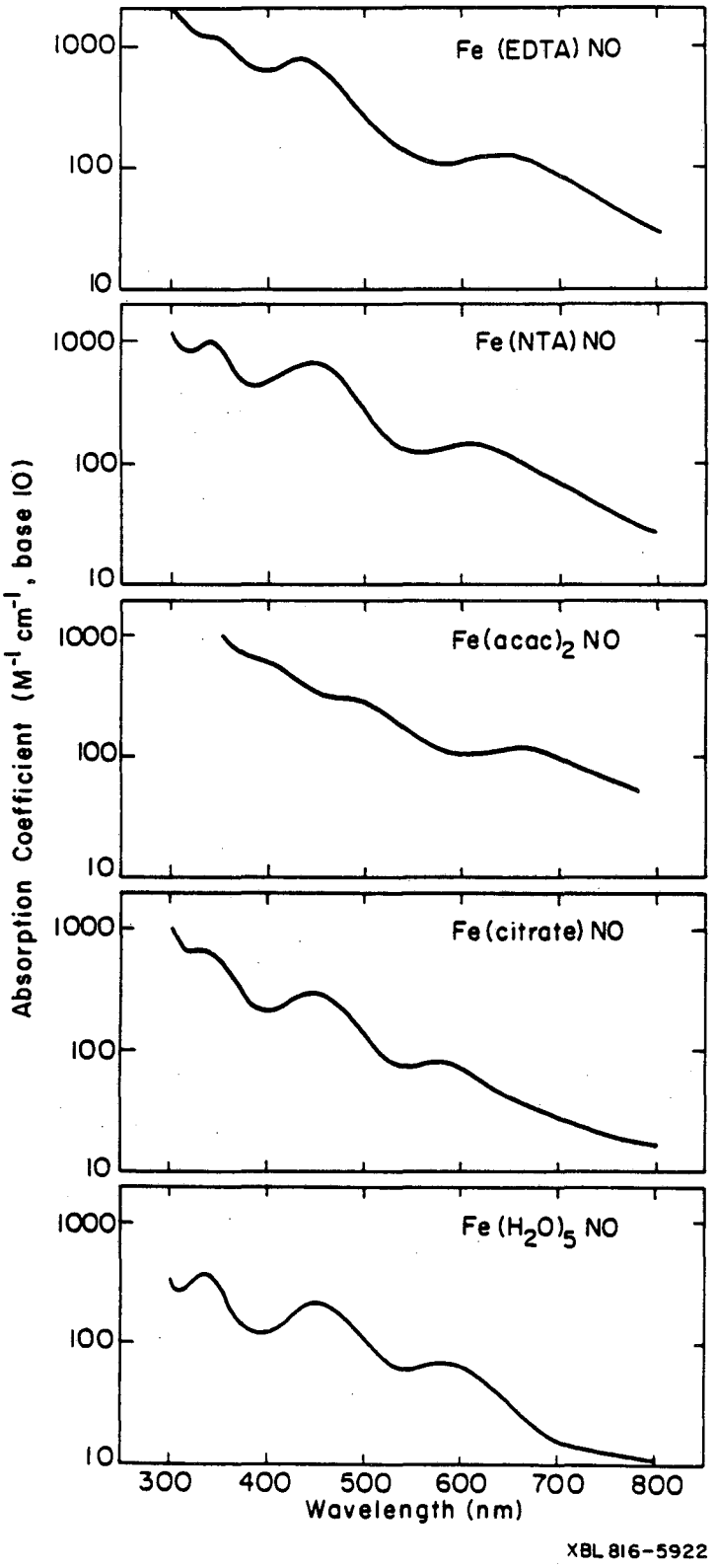

Fe (EDTA) NO
Fe (NTA) NO
Fe(acac)$_2$ NO
Fe(citrate) NO
Fe (H$_2$O)$_5$ NO
1000
100
10
Absorption Coefficient (M^{-1} cm^{-1}, base 10)
300
400
500
600
700
800
Wavelength (nm)
XBL 816-5922

Figure 4

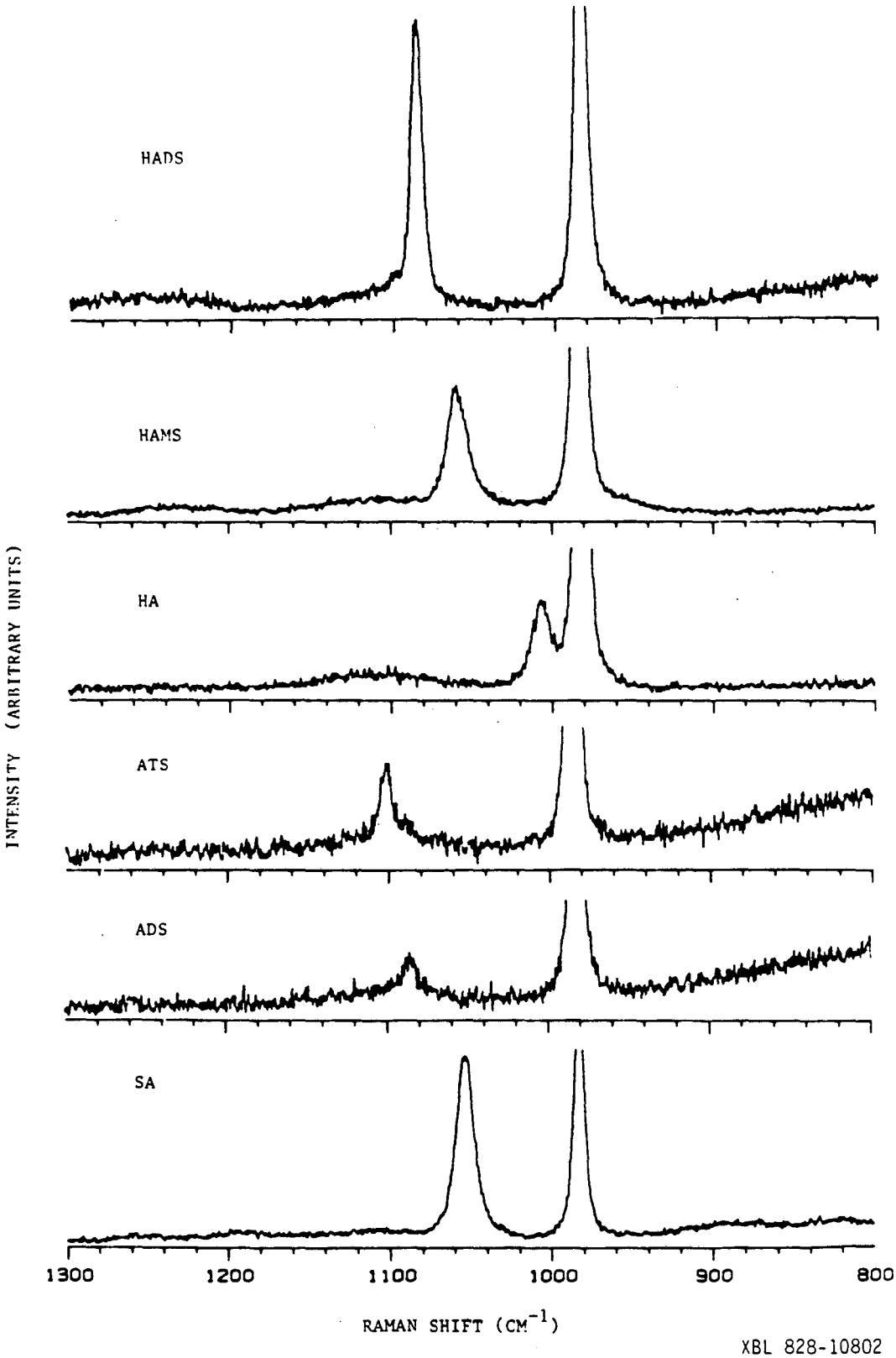
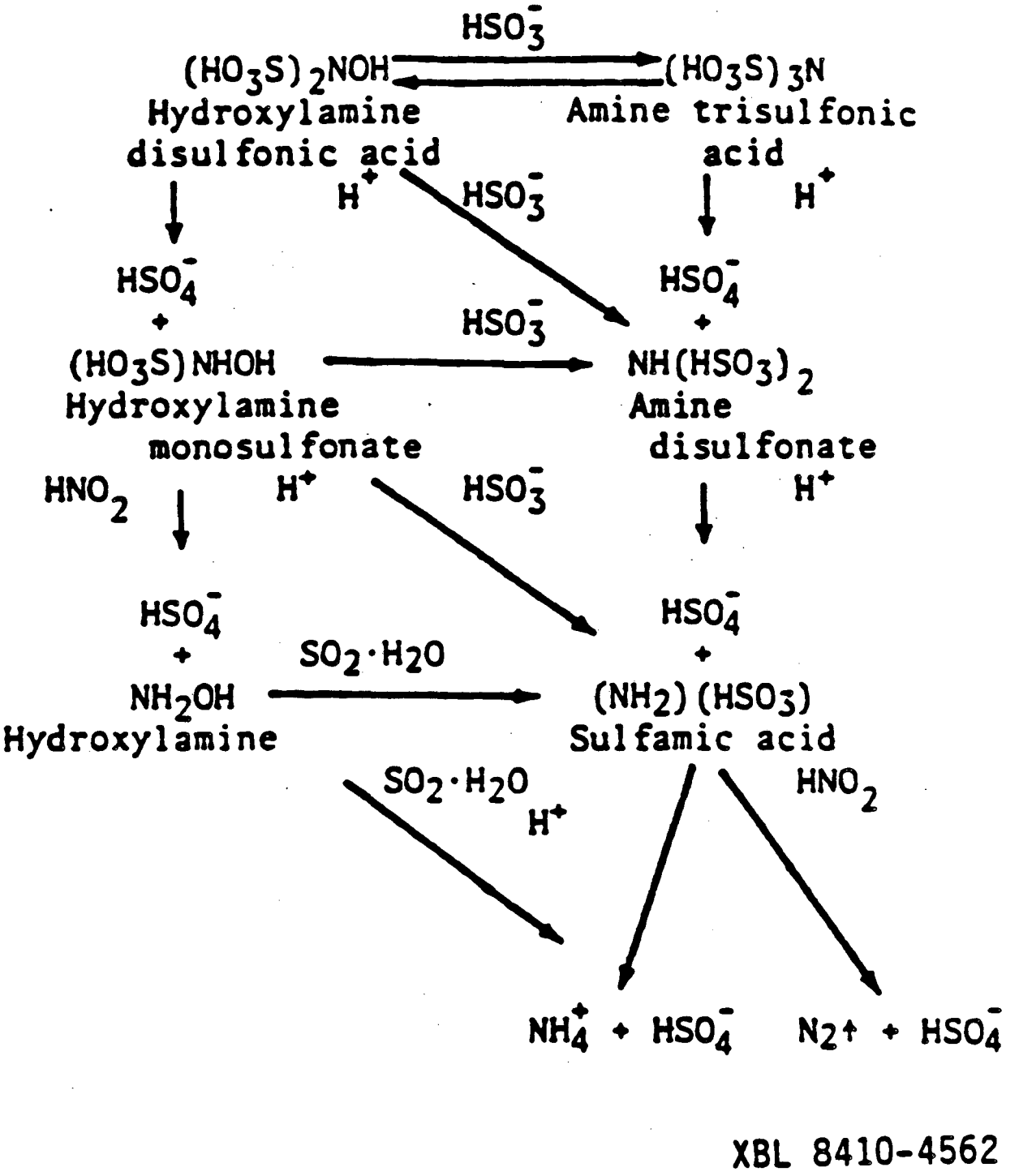

HADS
HAMS
HA
ATS
ADS
SA
INTENSITY (ARBITRARY UNITS)
1300
1200
1100
1000
900
800
RAMAN SHIFT (CM^{-1})
XBL 828-10802

Figure 5



XBL 8410-4562

Figure 6

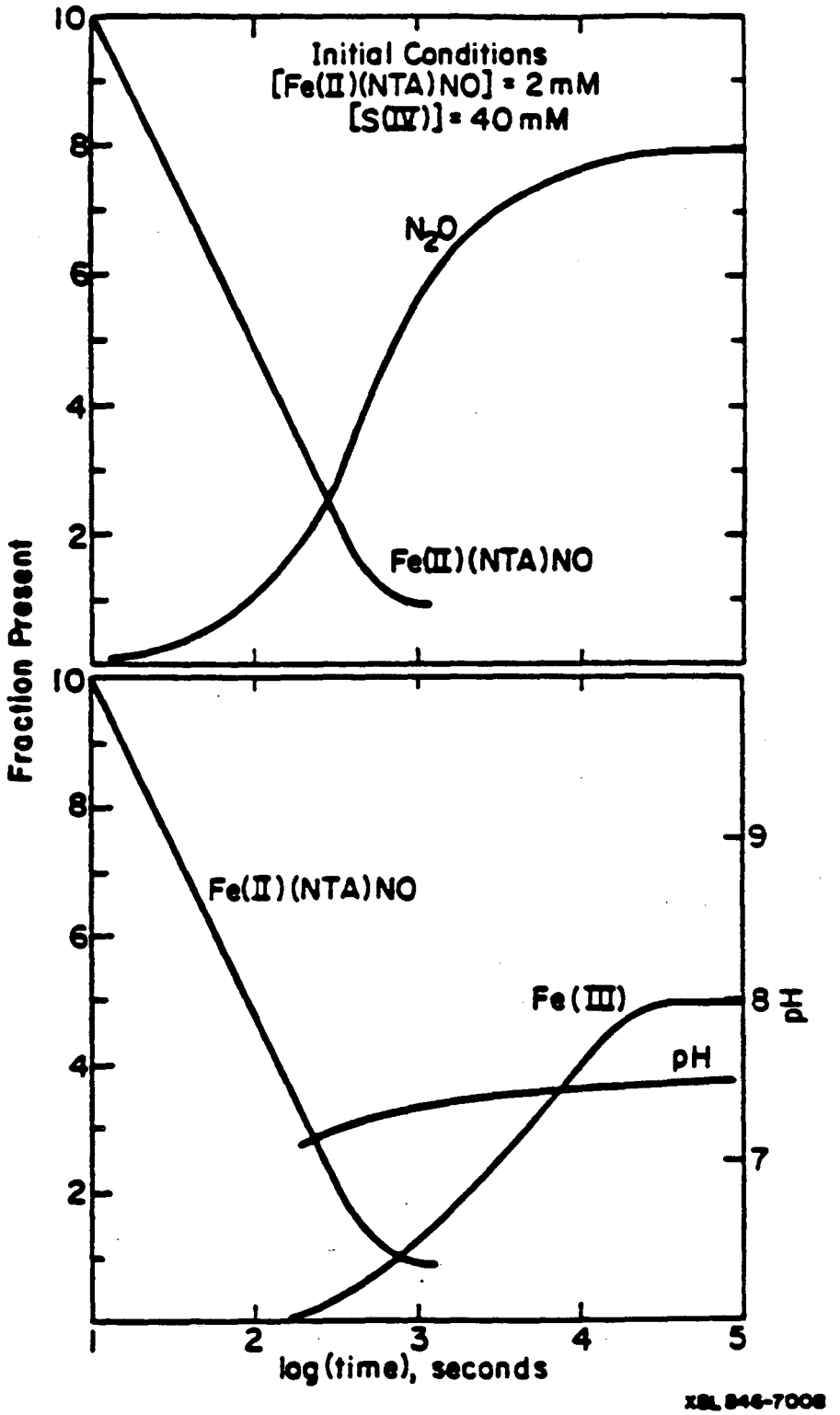

Initial Conditions
[Fe(II)(NTA)NO] = 2 mM
[S(IV)] = 40 mM
N2O
Fe(II)(NTA)NO
Fe(II)(NTA)NO
Fe(III)
pH
Fraction Present
pH
log (time), seconds
XBL 846-7008

Figure 7

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.

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