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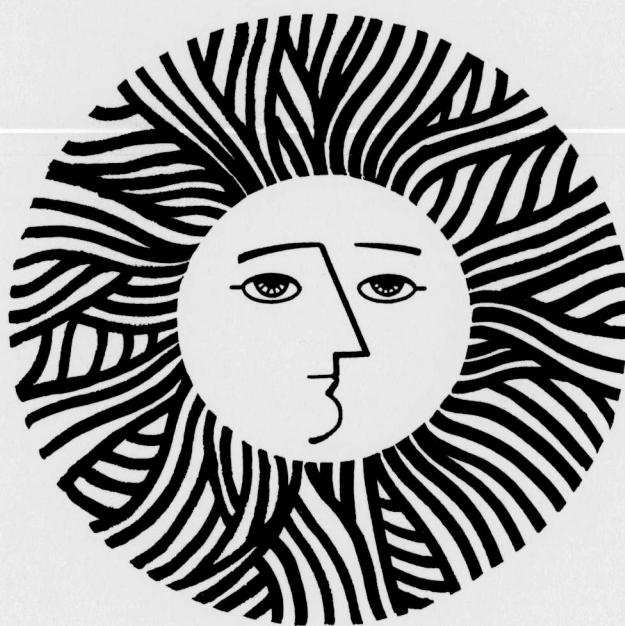
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REACTIONS OF SULFITE AND NITRITE IONS IN AQUEOUS  
SOLUTIONS

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## REACTIONS OF SULFITE AND NITRITE IONS IN AQUEOUS SOLUTIONS

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### I. Introduction

Lime/limestone scrubbers represent the current generation technology for power plant flue gas desulfurization (FGD). The important chemical reactions that take place after dissolution of flue gas in an aqueous lime/limestone slurry must be identified so that a scrubber with better performance and reliability can be constructed. Because power plant flue gas contains hundreds of ppm of both  $\text{SO}_2$  and  $\text{NO}_x$ , it is essential to understand the chemistry between  $\text{SO}_2$  and  $\text{NO}_x$  in aqueous solutions. This scientific understanding could also shed some light for the development of a wet simultaneous desulfurization and denitrification process based on the addition of reagents/additives to the existing lime or limestone FGD scrubbers.

We have reviewed the literature<sup>1-5</sup> and found that many concurrent and consecutive chemical reactions can occur as a result of the interaction between  $\text{NO}_x$  and  $\text{SO}_2$  in liquid water. The kinetics and mechanisms of these reactions have not been fully characterized. Nevertheless, it has been demonstrated that the products of the reaction depend on the concentrations of reactants, temperature, and acidity of the solution. For example, sulfuric acid is produced and  $\text{NO}_x$  is regenerated in the well-known lead chamber process<sup>1</sup> where the reaction is carried out at very low pH and high concentrations of reactants; while species such as  $\text{N}_2\text{O}$ , hydroxylamine sulfonates, amine sulfonates, and sulfuric

acids are produced<sup>2-5</sup> if the reaction takes place in a slightly acidic or neutral solution.

Nitrous (III) and nitric (V) acids are produced in the aqueous phase after nitrogen oxides are absorbed into liquid water, and sulfite/bisulfite ions (IV) are formed if  $\text{SO}_2$  dissolves in water. This paper reviews the kinetic studies of reactions that can take place as a result of interactions between sulfite/bisulfite ions S(IV) and nitrite ions (III) and presents the result of model calculations that give the concentration profile of species produced in this system as a function of reaction time. The effect of temperature, pH, and concentrations of reactant are shown.

## II. Review of Previous Kinetic Studies

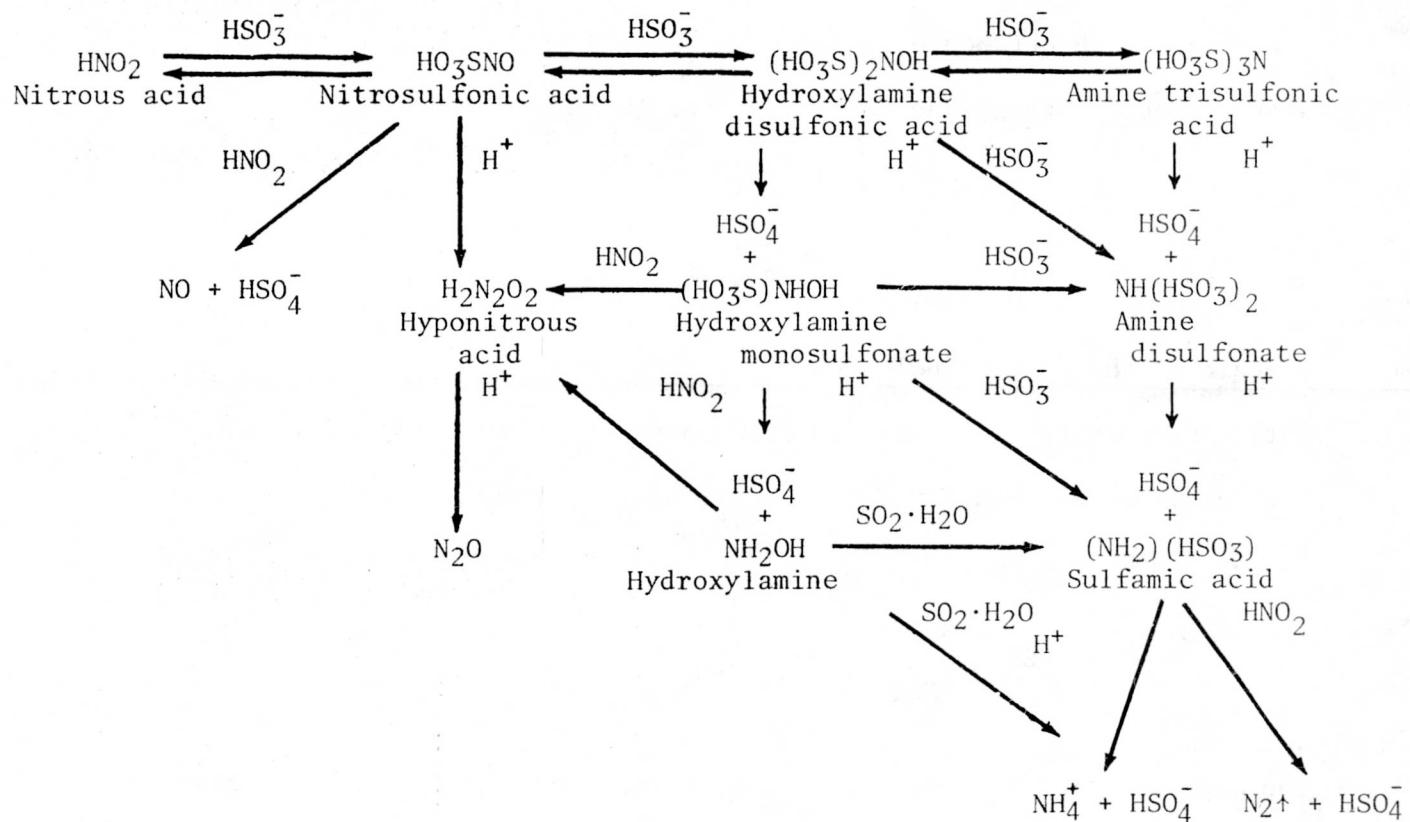
Nitrous acid and sulfite react to form nitrosulfonic acid, which then continues along one or more of three reaction paths:

1. Further sulfonation to produce hydroxylamine disulfonate and amine trisulfonate. These can hydrolyze to form sulfuric acid and reduced nitrogen species. The latter can undergo further reaction with bisulfite and nitrite.

2. Hydrolysis to form sulfuric acid and hyponitrous acid. The latter decomposes to produce nitrous oxide.

3. Reaction with nitrous acid to yield sulfuric acid and nitric oxide.

The extent to which these three different paths will contribute to the system depends on the pH, temperature, and concentration of nitrite and sulfite species. It is believed that process 1 favors a neutral or mildly acidic solution; processes 2 and 3 are expected to become increasingly important as the pH of the solution decreases. A summary of reactions that can take place as a result of interaction between sulfite and nitrite ions is shown in the following reaction scheme:



The kinetic information of reactions involved in this system is outlined below.

Formation of hydroxylamine disulfonate by reaction of nitrous acid with bisulfite ion. Hydroxylamine disulfonate (HADS) is formed according to the following net reaction:



The kinetics of this reaction was first studied (at pH between 5 and 7) by Seel and Degener<sup>6</sup> over two decades ago. They found two concurrent processes for the HADS production as summarized by the following rate law:

$$\frac{d[\text{HADS}]}{dt} = k_{1a} [\text{H}^+]^2 [\text{NO}_2^-] + k_{1b} [\text{H}^+] [\text{NO}_2^-] [\text{HSO}_3^-] . \quad (1)$$

Yamamoto and Kaneda<sup>7</sup> identified the same two processes. However, they found that the first term was really a combination of both general acid and acetic

acid specific catalyzed reactions. Seel and Knorre<sup>8</sup> later investigated this reaction (at pH between 6.13 and 6.92) and interpreted their results as a single process having the following rate law:

$$\frac{d[\text{HADS}]}{dt} = \frac{k_{2a} [\text{NO}_2^-] [\text{HSO}_3^-]^2}{1 + k_{2b} [\text{SO}_3^{2-}]} \quad (2)$$

Because of the discrepancies between these results, we have undertaken a systematic investigation<sup>4</sup> of this reaction over the pH range between 4.5 and 7. The reaction has been found to consist of two concurrent processes. The rate law was shown as

$$\frac{d[\text{HADS}]}{dt} = k_{3a} [\text{H}^+] [\text{NO}_2^-] [\text{HSO}_3^-] + k_{3b} [\text{NO}_2^-] [\text{HSO}_3^-]^2 \quad (3)$$

The dependence of  $k_{3a}$  and  $k_{3b}$  on temperature and ion strength was also studied:

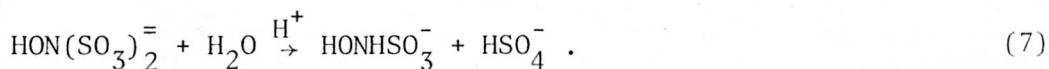
$$k_{3a} = 3.7 \times 10^{12} e^{-6100/T} \text{ liter}^2/\text{mole}^2\text{-sec} \quad (a)$$

$$k_{3b} = 9.0 \times 10^{-4} e^{2.1\sqrt{\mu}} \text{ liter}^2/\text{mole}^2\text{-sec} \quad (b)$$

The following reaction mechanism was suggested:



Hydrolysis of hydroxylamine disulfonate (HADS). HADS hydrolyzes to give hydroxylamine monosulfonate (HAMS) and sulfates:



The rate and mechanism of this hydrolysis was performed by Naiditch and Yost.<sup>9</sup>

These authors found that hydrolysis is catalyzed by acid as well as water, but the effect of water is much less than that of acid. The rate equation can be expressed as

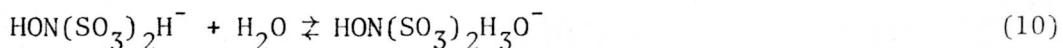
$$-\frac{d[HADS]}{dt} = \left\{ k_{8a}[H^+] + k_{8b}[H_2O] \right\} [HON(SO_3)_2^=] . \quad (8)$$

$k_{8a}$  and  $k_{8b}$  are respectively the rate constants for acid- and water-catalyzed reactions. At zero ionic strength:

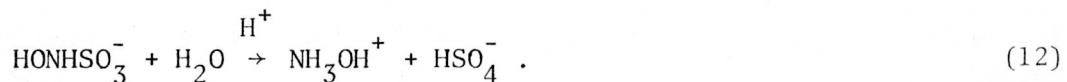
$$k_{8a} = 2.1 \times 10^{11} e^{-17600/RT} \text{ liter/mole-sec} \quad (c)$$

$$k_{8b} = 1.67 \times 10^{11} e^{-23000/RT} \text{ sec}^{-1} . \quad (d)$$

The proposed mechanism assumes that the ion  $HON(SO_3)_2H^-$  forms a reaction complex with water. The overall rate is determined by the rate at which the complex is converted into the hydrolytic products:



Hydrolysis of hydroxylamine monosulfonate (HAMS). HAMS hydrolyzes in acidic solution, but at a much slower rate than that of HADS.<sup>9</sup> The hydrolysis of HAMS produced hydroxylamine (HA) and sulfates:



The rate equation may be assumed to be

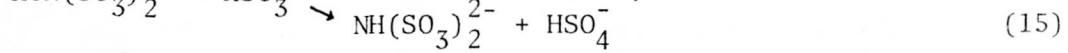
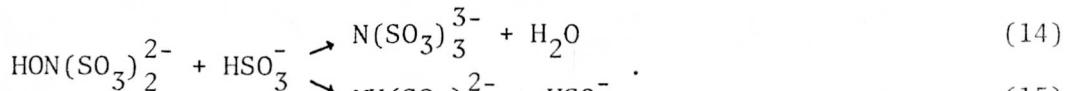
$$-\frac{d[HAMS]}{dt} = k [HONHSO_3^-] [H^+] . \quad (13)$$

The rate constant was not determined; however, an upper limit can be obtained from the result of Naiditch and Yost<sup>9</sup>:

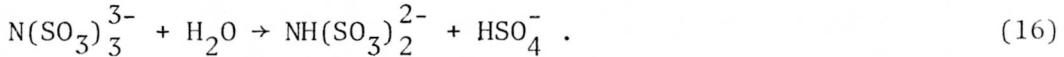
$$k \leq 2.65 \times 10^{11} e^{-19500/RT} \text{ liter/mole-sec} , \quad (e)$$

at an ionic strength  $\mu = 0.01 \text{ M}$ .

Sulfonylation of hydroxylamine disulfonate. Seel et al.<sup>10</sup> studied the reaction between HADS and bisulfite and found that this reaction produced about 70% aminetrisulfonate (ATS) and 30% aminedisulfonate (ADS) in the temperature range from 25 to 60°C, with reaction times ranging up to 4.5 hr at a pH of 7. The reaction proceeds according to Eqs. (14) and (15):



Aminedisulfonate can also be formed through the hydrolysis of hydroxylamine trisulfonate:



The rate of disappearance of HADS can be expressed as

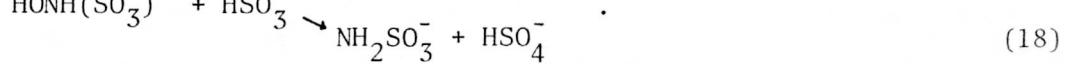
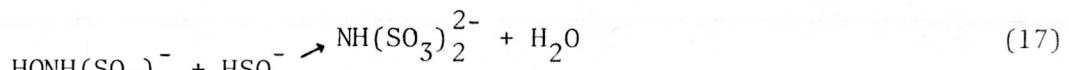
$$-\frac{d[\text{HADS}]}{dt} = Ae^{-\Delta E_a/RT} [\text{HON}(\text{SO}_3)^{2-}] [\text{HSO}_3^-] , \quad (f)$$

where  $A = 7.2 \times 10^9 \text{ liter/mole-sec}$ , and  $\Delta E_a = 18.0 \text{ kcal/mole}$ . This rate equation indicates that the rate determining step is reaction 14 and/or 15, while Eq. (16) is a fast reaction; and the activation energy determined is a weighted value of reactions 7, 8, and 9, leading to the formation of a mixture of products.

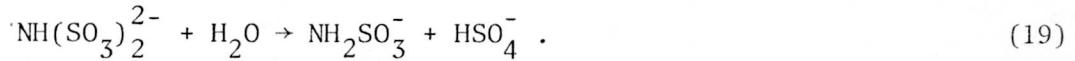
Yamamoto and Kaneda<sup>7</sup> measured the rate of formation of ATS and obtained an identical rate equation with  $A = 3.4 \times 10^{10} \text{ liter/mole-sec}$ , and  $\Delta E_a =$

19.2 kcal/mole at an ionic strength  $\mu = 1.0$  M.

Sulfonylation of hydroxylamine monosulfonate (HAMS). According to Seel et al.,<sup>10</sup> the reactions between HAMS and bisulfite are branched ones (Eqs. 17 and 18), producing about 70% aminedisulfonate (ADS) and 30% sulfamate (SAM) in the temperature range 25-60°C, with reaction times ranging up to 12 hr at a pH of 7:



Aminedisulfonate can undergo hydrolysis to form sulfamate:



The rate determining step is reaction 17 and/or 18. The rate equation is:

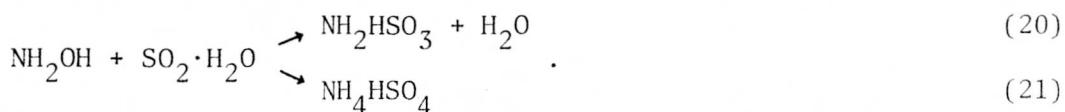
$$-\frac{d[\text{HAMS}]}{dt} = Ae^{-\Delta E_a/RT} [\text{HONH}(\text{SO}_3)^-], \quad (g)$$

where  $A = 2.0 \times 10^{13}$  liter/mole-sec, and  $\Delta E_a = 24.5$  kcal/mole. Hydroxylamine O-sulfinic acids are assumed to be intermediate products.

Sulfonylation of hydroxylamine (HA). Sisler and Audrieth<sup>11</sup> studied the formation of sulfamic acid by the reaction of hydroxylamine with sulfur dioxide in an aqueous solution and proposed that the reaction mechanism involved coordination between  $\text{NH}_2\text{OH}$  and  $\text{SO}_2$  molecules with subsequent rearrangement to sulfamic acid. The kinetics of this reaction was investigated by Brackman and Higginson<sup>12</sup> at room temperature. They found that in addition to sulfamic acid, trace amounts of ammonium bisulfate were also formed and that the percentage of ammonium bisulfate produced appeared to be independent of pH. Fraser<sup>13</sup> and Gomiscek et al.<sup>14</sup> studied the kinetics of this reaction as a

function of temperature. The kinetic studies by both Brackman and Higginson<sup>12</sup> and Fraser<sup>13</sup> were performed by monitoring the rate of disappearance of total sulfite during the course of the reaction, while Gomiscek et al.<sup>14</sup> studied this reaction by monitoring the rate of disappearance of total hydroxylamine.

This reaction can be expressed as



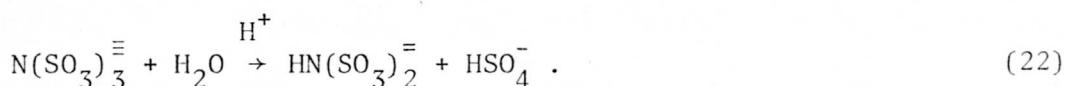
The rate law can be written as

$$-\frac{d[\text{HA}]}{dt} = (k_{20} + k_{21}) [\text{NH}_2\text{OH}] [\text{SO}_2 \cdot \text{H}_2\text{O}] \quad (h)$$

The enthalpy and entropy of activation for the formation of sulfamic acid and ammonium bisulfate are:

	Sulfamic acid		Ammonium bisulfate	
	$\Delta H_{20}^{\ddagger}$ (kcal/mole)	$\Delta S_{20}^{\ddagger}$ (e.u)	$\Delta H_{21}^{\ddagger}$ (kcal/mole)	$\Delta S_{21}^{\ddagger}$ (e.u)
Fraser <sup>13</sup>	10.9	-16	1	-56
Gomiscek et al. <sup>14</sup>	13.4	- 6.1	3	-45.8

Hydrolysis of aminetrisulfonate (ATS). The hydrolysis of potassium aminetrisulfonate has been studied by Sisler and Audrieth<sup>11</sup> at 25, 40, 67, and 100°C. They found that this reaction (Eq. 22) is acid catalyzed and that the ATS was rapidly converted into aminedisulfonate and sulfates even in a neutral solution and at 25°C:

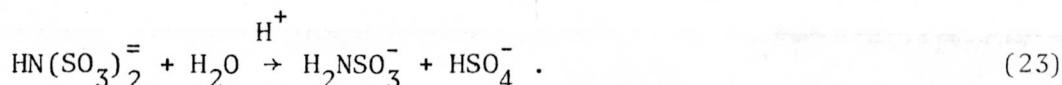


The rate equation may be written as



The rate constant has not been determined however.

Hydrolysis of amine disulfonates (ADS). ADS hydrolyzes irreversibly and quantitatively to form sulfamate (SFM) and sulfates according to Eq. (23)<sup>15-17</sup>:



The rate of the acid-catalyzed reaction has been studied<sup>17</sup> over the temperature range 25-45°C. The results at constant ionic strength conform to the rate equation:



The variation of the rate constant  $k_{23}$  at zero ionic strength with temperature is described by the equation

$$k_{23} = 2.54 \times 10^{14} e^{-23500/RT} \text{ liter/mole-sec} .$$

The relatively large value of the frequency factor was explained on the basis of a large positive entropy ( $\Delta S^{\neq} = 21.3$  e.u.) of formation of the activated complex due to its electrostatic interaction with the solvent.

The dependence of the specific rate constant on ionic strength at 25°C, based on the Brønsted-Debye-Hückel theory,<sup>18</sup> (k) was studied.

$$\log_{10} k_{23} = \log_{10} k_{23}^{\circ} + \frac{\frac{2Az_1z_2\mu}{1+\mu}^{1/2}}{1/2} + \beta\mu , \quad (\text{k})$$

where  $A = 0.5065$ ,  $z_1z_2 = -2$ , and  $\beta\mu = +0.092$ .

The uncatalyzed hydrolysis was found to have an undetectable rate compared to the rate of the acid-catalyzed reaction.

The ionization constant for reaction 23,



in a sodium chloride solution at an ionic strength of 1.0 at 25°C is  $3.2 \times 10^{-9}$  mole/liter.

Hydrolysis of sulfamate (SAM). The kinetics of hydrolysis of sulfamate ion was investigated by Maron and Berens<sup>19</sup> (in dilute acid at 80-98°C) and by Candlin and Wilkins<sup>20</sup> (in  $10^{-3}$  M to 6 M perchloric acid at 95°C). A reaction mechanism involving a pre-equilibrium between sulfamate ion and sulfamic acid (Eq. 24), followed by slow hydrolysis of the acid (Eq. 25), was proposed:



The rate equation can be expressed as

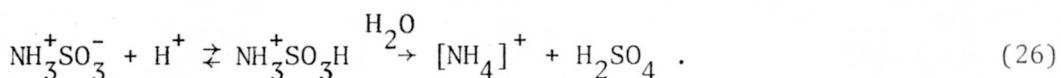
$$-\frac{d[\text{SAM}]}{dt} = \frac{k[\text{H}^+]}{K + [\text{H}^+]} [\text{NH}_2\text{SO}_3^- + \text{NH}_2\text{SO}_3\text{H}], \quad (1)$$

where  $k = 2.3 \times 10^{-4} \text{ sec}^{-1}$  at 95°C, and  $K$  is the ionization constant of sulfamic acid, which has been determined by E.M.F.<sup>21</sup> and conductance<sup>22</sup> measurements. A relationship,  $-\log K = (3792.8/T) - 24.122 + 0.041544 T$ , has been deduced from the measurements between 10 and 50°C ( $K = 0.1$  mole/liter at 25°C, and 0.266 at 95°C).

The energies and entropies of activation determined by Maron and Berens<sup>19</sup> (30.5 kcal/mole and 9.7 u.e.) include the energy and entropy of formation of sulfamic acid (i.e., both reactions 24 and 25). The latter values can be

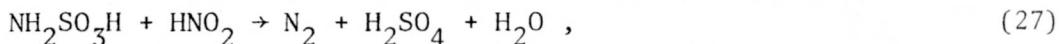
estimated from the data of King and King<sup>21</sup> as +0.9 kcal/mole and +9 e.u., and this will mean values for the energy and entropy of activation of hydrolysis of sulfamic acid (Eq. 25) of 29.6 kcal/mole and 0.7 e.u. respectively, which are in good agreement with those determined by Candlin and Wilkins<sup>20</sup> (29.7 kcal/mole and 3.2 e.u.).

In addition to the A 1 acid-catalyzed decomposition of sulfamate ion, proposed by Maron and Berens<sup>19</sup> and Candlin and Wilkins,<sup>20</sup> Hughes and Lusty<sup>23</sup> present evidence that an additional A 2 path involving sulfamic acid (Eq. 26) also occurs:

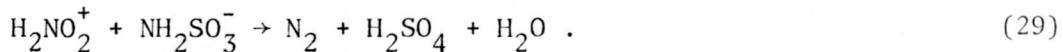


This mechanism would predominate or occur exclusively above 2 M perchloric acid.

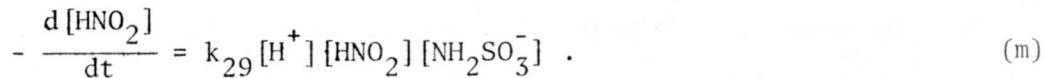
Reaction of sulfamic acid with nitrous acid. A kinetic study of the reaction of sulfamic acid with nitrous acid (Eq. 27) by Hughes<sup>24</sup> revealed that the mechanism



at acidities less than 0.248 M, proceeded according to reactions 28 and 29:



The protonated nitrous acid species reacts with sulfamate ion in a slow step. The rate equation can be written as



At an ionic strength  $\mu = 0.25$  M,  $k_{29}$  is 170, 667, 1130, and 2040 liter<sup>2</sup> mole<sup>-2</sup> sec<sup>-1</sup> at 0, 18, 25, and 34.5°C respectively. This temperature dependence study reveals that  $\Delta S^\circ = -6.6$  e.u., and  $\Delta H^\circ = 11.3$  kcal/mole.

In the acid range 0.25-3 M, a second pathway emerges in which  $\text{H}_2\text{NO}_2^+$  attacks sulfamic acid. As the concentration of sulfamate ion becomes very small at these higher acidities, so the reaction with sulfamic acid will become more important although sulfamate ion is more reactive than sulfamic acid. The two mechanisms are operating side by side, with an increase of acidity favoring the reaction through sulfamic acid.

Many more reactions are known to take place in this system in addition to those discussed above. However, their kinetics and mechanisms have not been well characterized. Some of these reactions are:

1. Formation of hyponitrous acid ( $\text{H}_2\text{N}_2\text{O}_2$ ) from the acid-catalyzed hydrolysis of nitrosulfonic acid
2. Reaction of nitrosulfonic acid with nitrous acid to form sulfates and liberate NO
3. Production of hyponitrous acid and sulfates from the reaction of hydroxylamine monosulfonate with nitrous acid
4. Reaction of hydroxylamine with nitrous acid to yield hyponitrous acid or  $\text{N}_2\text{O}$
5. Reaction of hyponitrous acid with nitrous acid to form nitric acid and  $\text{N}_2$ .

### III. Chemical Kinetics Modeling

The concentration profiles of HADS, HAMS, HA, ATS, ADS, SAM,  $\text{NH}_4^+$ ,  $\text{N}_2$ , and sulfate as a function of time resulting from the reaction of sulfite and nitrite ions in aqueous solutions was calculated at various conditions (Figs. 1-6). A CHEMK software package developed by Systems Applications, Inc., of

San Rafael, California, was used for this computation. Three different initial  $\text{SO}_2$  and  $\text{NO}_x$  concentrations were considered (in ppm): 1000, 450, and 50; 1000, 250, and 250; 2000, 250, and 250 respectively for  $\text{SO}_2$ ,  $\text{NO}$ , and  $\text{NO}_2$ . Calculations were carried out at two different temperatures (55 and 25°C) and three different pH's (3, 5, and 7). The pH of the solution was assumed to be constant throughout the reaction. Table 1 lists elementary reactions considered and rate constants used. The following additional assumptions were made in this calculation:

1. Gas dissolution and liberation rates are much larger than chemical reaction rates.
2. Any reaction involving  $\text{HNO}_3$ ,  $\text{NO}(\ell)$ ,  $\text{NO}_2(\ell)$ ,  $\text{N}_2\text{O}_3(\ell)$ , and  $\text{N}_2\text{O}_4(\ell)$  is neglected.
3. The equilibrium is maintained all the time for the following reaction pairs: 3, 4; 10, 11; 12, 13; 14, 15; and 16, 17. The rate constant of these 10 reactions was adjusted to satisfy the equilibrium condition.
4. Oxidation of  $\text{NO}$  to  $\text{NO}_2$  (both in gas phase and aqueous solution) is discounted.

Figures 1-4, 5, and 6 show the time-resolved concentration of species in a batch reactor at various pH's, temperatures, and initial partial pressures of  $\text{SO}_2$  and  $\text{NO}_x$  for the first 2 and 24 hours respectively. The gas to liquid ratio (G/L) is 75. Figure 1 (at  $P_{\text{SO}_2} = 1000$ ,  $P_{\text{NO}} = 450$ , and  $P_{\text{NO}_2} = 50$  ppm, pH = 5, and T = 328°K) demonstrated that the removal efficiency of NO is only about 10%, although  $\text{NO}_2$  can be removed nearly completely. This is because NO alone cannot be converted into nitrous acid. The major product is HADS within the initial 1-1/2 hr; the concentrations of HAMS and sulfate increase while that of HADS decreases as the reaction time continues. If the reaction is allowed to continue, the final products will be  $\text{NH}_4^+$ ,  $\text{N}_2$ , and sulfate.

Because we disregard the reaction of HAMS and HA with  $\text{HNO}_2$  and the hydrolysis of nitrosulfonic acid, no  $\text{N}_2\text{O}$  is formed.

The effect of the oxidation of NO to  $\text{NO}_2$  on the reaction is illustrated in Fig. 2 ( $\text{PSO}_2 = 1000$ ,  $\text{P}_{\text{NO}} = \text{P}_{\text{NO}_2} = 250 \text{ ppm}$ ,  $\text{pH} = 5$ , and  $T = 328^\circ\text{K}$ ). The result indicates enormous improvement in  $\text{NO}_x$  removal efficiency. The concentration of HADS, HAMS, ATS, etc., species is larger (compared to Fig. 1) because of the larger concentration of nitrite/nitrous acid in the solution. By the same token,  $\text{HSO}_3^-$  is consumed at a larger rate.

The effect of the pH of the solution on the reaction is shown in Fig. 3 ( $\text{PSO}_2 = 1000$ ,  $\text{P}_{\text{NO}} = \text{P}_{\text{NO}_2} = 250 \text{ ppm}$ ,  $\text{pH} = 3$ , and  $T = 328^\circ\text{K}$ ). The reactions speed up at a lower pH (between  $\text{pH} = 5$  and 3), and  $\text{NO}_x$  is reduced at a larger rate. The concentration of HAMS is larger than HADS after about 20 min. Similarly, larger concentrations of HA, SAM,  $\text{N}_2$ , and  $\text{NH}_4^+$  are observed at a given time. These are due to the fact that the hydrolysis reaction is acid catalyzed, and therefore low pH conditions would favor the formation of hydrolysis products.

If the concentration of  $\text{SO}_2$  is increased while that of  $\text{NO}_x$  is held constant, i.e., at a larger  $\text{SO}_2/\text{NO}_x$  ratio (Fig. 4, with  $\text{PSO}_2 = 2000$ ,  $\text{P}_{\text{NO}} = \text{P}_{\text{NO}_2} = 250 \text{ ppm}$ ,  $\text{pH} = 5$ , and  $T = 328^\circ\text{K}$ ), the production rate of ATS, ADS, and SAM increases because the larger  $\text{SO}_2/\text{NO}_x$  ratio favors sulfonation reactions. It is interesting to note that  $\text{NH}_4^+$  to  $\text{N}_2$  ratio increases with the increase of the  $\text{SO}_2$  to  $\text{NO}_x$  ratio because the rate of formation of  $\text{N}_2$  is only slightly affected by the change in  $\text{SO}_2$  to  $\text{NO}_x$  ratio. (The effect due to the increases in SAM concentration is offset by that due to the decrease in  $\text{HNO}_2$  concentration.) However, the rate of formation of  $\text{NH}_4^+$  increases as the concentration of SAM increases at a constant pH of the solution.

The effect of temperature is demonstrated in Fig. 5 ( $P_{SO_2} = 1000$ ,  $P_{NO} = P_{NO_2} = 250$  ppm, pH = 5, and T = 328°K) and Fig. 6 ( $P_{SO_2} = 1000$ ,  $P_{NO} = P_{NO_2} = 250$  ppm, pH = 5, and T = 298°K). The results indicate that the overall reaction rate speeds up at higher temperatures. Fig. 7 shows that some reduced nitrogen species identical to those discussed in this paper have been identified in a few flue-gas wet simultaneous desulfurization and denitrification processes based on both oxidation-absorption-reduction and absorption-reduction principles.

Further exploration of reagent/additives to promote the absorption of relatively insoluble NO in aqueous solution and investigation of the kinetics of reactions subsequently involved in the system could permit the simultaneous removal of  $NO_x$  in lime/limestone FGD scrubbers without requiring major capital investment.

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Table I. Reactions considered and rate constants used for modeling.

Reaction	$k, K, \text{ or } H (298^\circ\text{K})^a$	$\Delta E_a$ (kcal/mole)
1. $\text{SO}_2(g) \xrightleftharpoons{\text{H}_2\text{O}} \text{SO}_2 \cdot \text{H}_2\text{O}$	1.24	
2. $\text{SO}_2 \cdot \text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{HSO}_3^-$	$1.27 \times 10^{-2}$	
3. $\text{HSO}_3^- \rightleftharpoons \text{H}^+ + \text{SO}_3^{2-}$	$6.24 \times 10^{-8}$	
4. $2\text{HSO}_3^- \rightleftharpoons \text{S}_2\text{O}_5^{2-} + \text{H}_2\text{O}$	$7.0 \times 10^{-2}$	
5. $\text{NO}(g) + \text{NO}_2(g) \xrightleftharpoons{\text{H}_2\text{O}(g)} 2\text{HNO}_2(g)$	$5.31 \times 10^{-2}$	
6. $\text{HNO}_2(g) \xrightleftharpoons{\text{H}_2\text{O}} \text{HNO}_2$	49	
7. $\text{HNO}_2 \rightleftharpoons \text{H}^+ + \text{NO}_2^-$	$5.1 \times 10^{-4}$	
8. $\text{H}^+ + \text{HNO}_2 \rightarrow \text{NO}^+ + \text{H}_2\text{O}$	$4.08 \times 10^2$	11.5
9. $\text{NO}^+ + \text{HSO}_3^- \rightarrow \text{NOSO}_3^- + \text{H}^+ \text{ b}$		
10. $\text{HNO}_2 + \text{HSO}_3^- \rightarrow \text{NOSO}_3^- + \text{H}_2\text{O}$	2.43	12.1
11. $\text{NOSO}_3^- + \text{HSO}_3^- \rightarrow \text{HON}(\text{SO}_3)^{2-} \text{ b}$		
12. $\text{NO}_2^- + \text{S}_2\text{O}_5^{2-} \rightarrow \text{ON}(\text{SO}_3)^{3-} \text{ b}$	$1.29 \times 10^{-2}$	
13. $\text{ON}(\text{SO}_3)^{3-} + \text{H}^+ \rightarrow \text{HON}(\text{SO}_3)^{2-} \text{ b}$		
14. $\text{HON}(\text{SO}_3)^{2-} + \text{H}^+ \xrightleftharpoons{\text{H}_2\text{O}} \text{HONHSO}_3^- + \text{H}^+ + \text{HSO}_4^-$	$1.92 \times 10^{-2}$	17.6
15. $\text{HON}(\text{SO}_3)^{2-} \xrightleftharpoons{\text{H}_2\text{O}} \text{HONHSO}_3^- + \text{HSO}_4^-$	$1.52 \times 10^{-6}$	23.0
16. $\text{HONHSO}_3^- + \text{H}^+ \xrightleftharpoons{\text{H}_2\text{O}} \text{NH}_2\text{OH} + \text{H}^+ + \text{HSO}_4^-$	$9.45 \times 10^{-4}$	19.5
17. $\text{HON}(\text{SO}_3)^{2-} + \text{HSO}_3^- \rightarrow \text{N}(\text{SO}_3)^{3-} + \text{H}_2\text{O}$	$2.02 \times 10^{-4}$	19.2

Table I (contd.)

Reaction	$k, K, \text{ or } H (298^\circ K)^a$	$\Delta E_a$ (kcal/mole)
18. $\text{N}(\text{SO}_3)_3^{3-} + \text{H}^+ \xrightarrow{\text{H}_2\text{O}} \text{HN}(\text{SO}_3)_2^{2-} + \text{HSO}_4^-$ <sup>b</sup>		
19. $\text{HN}(\text{SO}_3)_2^{2-} + \text{H}^+ \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{NSO}_3^- + \text{HSO}_4^-$	$9.85 \times 10^{-4}$	23.5
20. $\text{HON}(\text{SO}_3)_2^{2-} + \text{HSO}_3^- \rightarrow \text{N}(\text{SO}_3)_3^{3-} + \text{H}_2\text{O}$	$2.84 \times 10^{-4}$	18.0
21. $\text{HON}(\text{SO}_3)_2^{2-} + \text{HSO}_3^- \rightarrow \text{HN}(\text{SO}_3)_2^{2-} + \text{HSO}_4^-$	$1.22 \times 10^{-4}$	18.0
22. $\text{HONHSO}_3^- + \text{HSO}_3^- \rightarrow \text{HN}(\text{SO}_3)_2^{2-} + \text{H}_2\text{O}$	$1.50 \times 10^{-5}$	24.5
23. $\text{HONHSO}_3^- + \text{HSO}_3^- \rightarrow \text{H}_2\text{NSO}_3^- + \text{HSO}_4^-$	$6.44 \times 10^{-6}$	24.5
24. $\text{NH}_2\text{OH} + \text{SO}_2 \cdot \text{H}_2\text{O} \rightarrow \text{H}_2\text{NSO}_3^- + \text{H}_2\text{O} + \text{H}^+$	$2.58 \times 10^1$	13.4
25. $\text{NH}_2\text{OH} + \text{SO}_2 \cdot \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{HSO}_4^-$	$6.7 \times 10^{-1}$	3
26. $\text{H}_2\text{NSO}_3^- + \text{HONO} \rightarrow \text{N}_2 + \text{HSO}_4^- + \text{H}_2\text{O}$	$1.13 \times 10^2$	11.3

<sup>a</sup>Units are mole liter<sup>-1</sup> for aqueous species and atm for gaseous species.

<sup>b</sup>Rate constants of 9, 11, 13, and 18 are assumed to be fast.

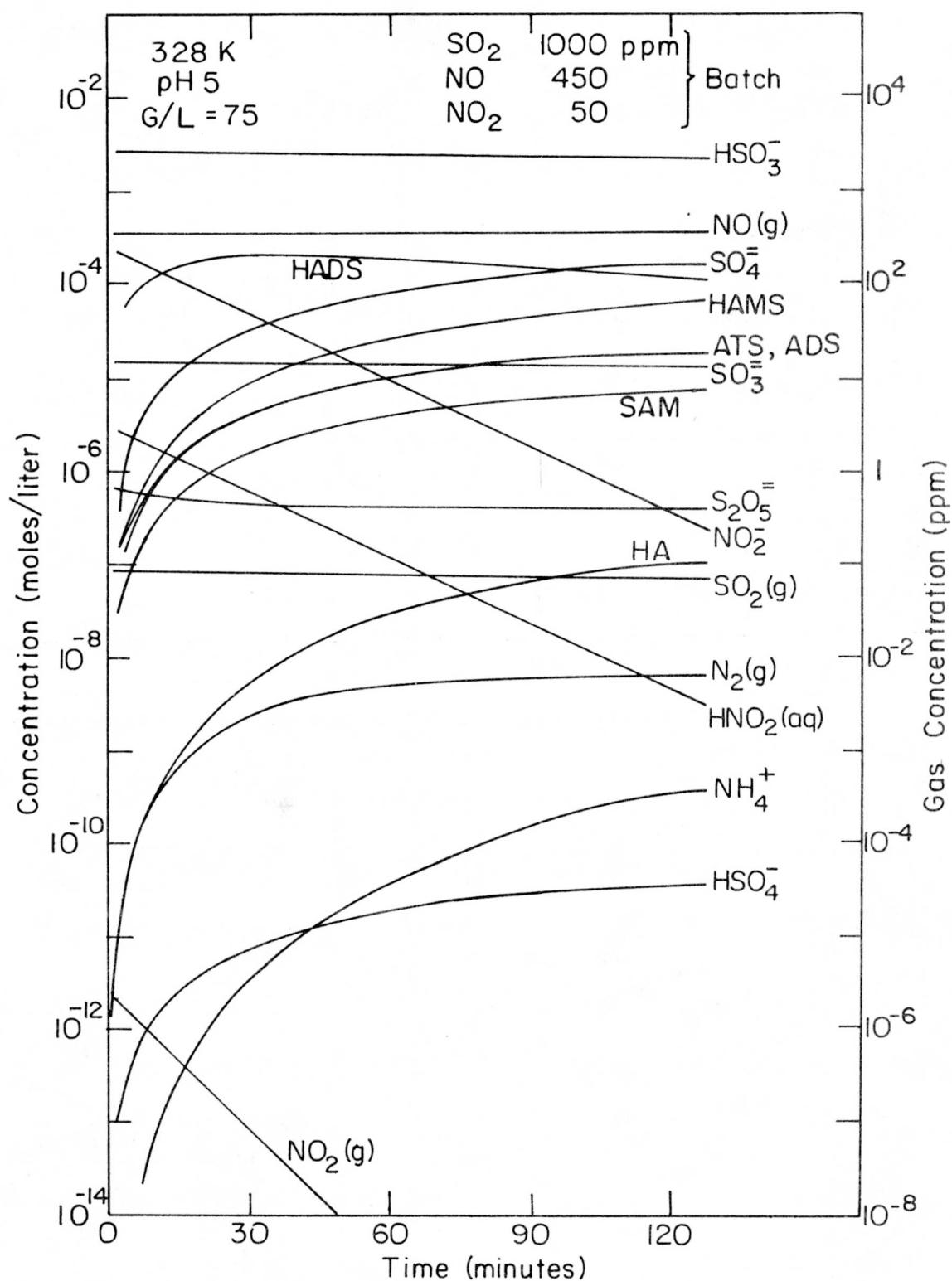
Table II. Some reduced nitrogen species identified in a few flue gas wet simultaneous desulfurization and denitrification processes.

Process	Additives	Reduced nitrogen species identified	NO <sub>x</sub> removal efficiency
Asahi	Na <sub>2</sub> SO <sub>3</sub> , Fe <sup>+2</sup> (EDTA)	NH(SO <sub>3</sub> NA) <sub>2</sub> , N <sub>2</sub>	60-85
Chisso	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>3</sub> , Fe <sup>+2</sup> (PCC)*	NH(SO <sub>3</sub> NH <sub>4</sub> ) <sub>2</sub> , NH <sub>2</sub> (SO <sub>3</sub> NH <sub>4</sub> ), (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	60-85
Chiyoda	O <sub>3</sub>	N <sub>2</sub> O, N <sub>2</sub>	80-90
Ishikawajima- Harima	O <sub>3</sub>	Ca(NH <sub>2</sub> SO <sub>3</sub> ) <sub>2</sub> , N <sub>2</sub>	80-90
Mitsubishi	O <sub>3</sub>	Ca[NH(SO <sub>3</sub> ) <sub>2</sub> ], Ca[NOH(SO <sub>3</sub> ) <sub>2</sub> ], NH <sub>2</sub> OH, N <sub>2</sub> O, N <sub>2</sub>	80-90

\* PCC stands for proprietary chelating compound.

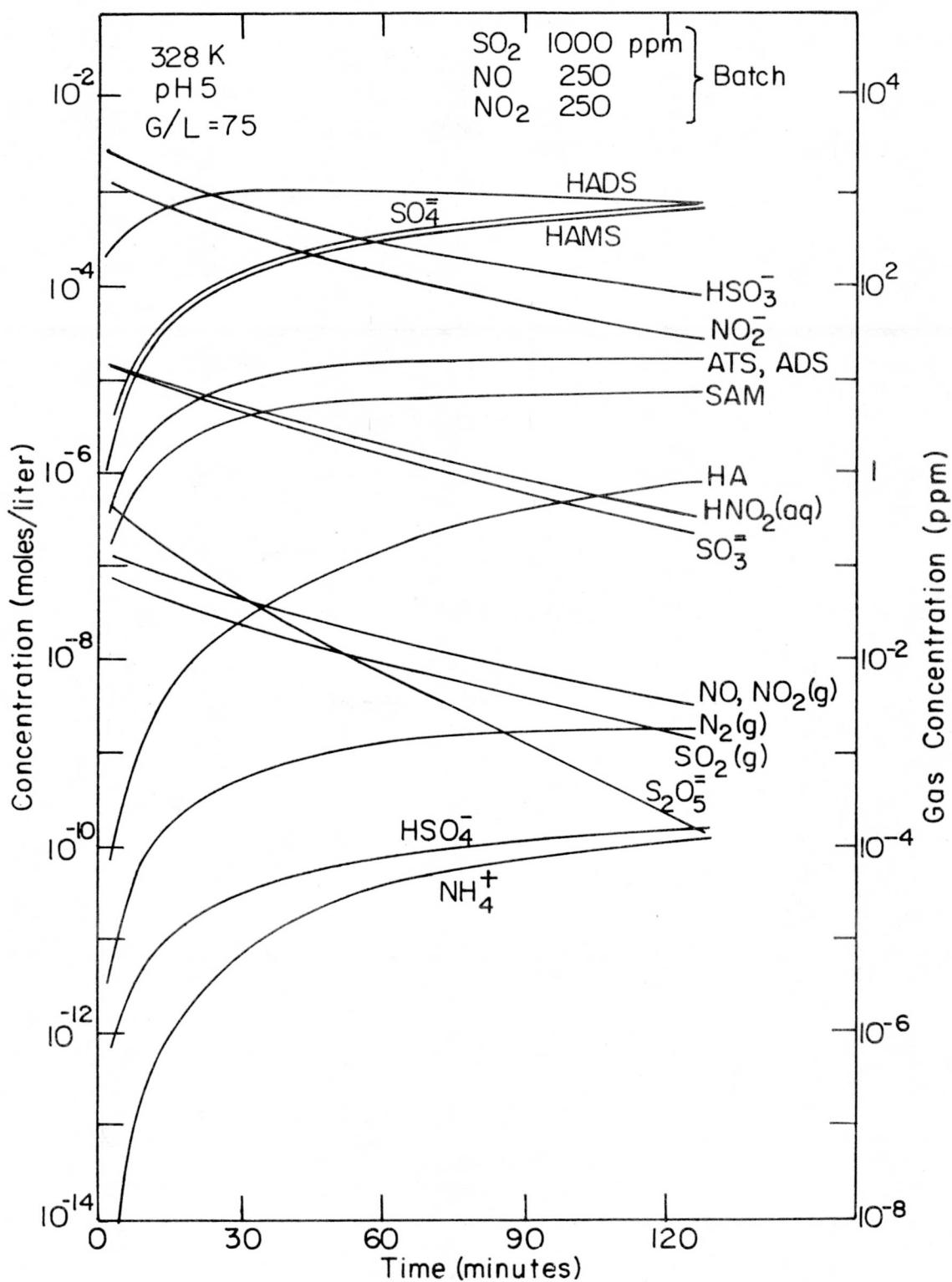
Figure captions

1. The concentration profile of species as a function of reaction time in a batch reactor (pH=5 and temp.=328 K) at the following initial condition:  $P_{SO_2} = 1000$ ,  $P_{NO} = 450$ , and  $P_{NO_2} = 50$  ppm. The gas to liquid ratio ,G/L is 75.
2. The concentration profile of species as a function of reaction time in a batch reactor (pH=5 and temp.=328 K) at the following initial condition:  $P_{SO_2} = 1000$ ,  $P_{NO} = P_{NO_2} = 250$  ppm. The gas to liquid ratio, G/L is 75.
3. The concentration profile of species as a function of reaction time in a batch reactor (pH=3 and temp.=328 K) at the following initial condition:  $P_{SO_2} = 1000$ ,  $P_{NO} = P_{NO_2} = 250$  ppm. The gas to liquid ratio, G/L is 75.
4. The concentration profile of species as a function of reaction time in a batch reactor (pH=5 and temp.=328 K) at the following initial condition:  $P_{SO_2} = 2000$ ,  $P_{NO} = P_{NO_2} = 250$  ppm. The gas to liquid ratio ,G/L is 75.
5. The concentration profile of species as a function of reaction time in a batch reactor (pH=5 and temp.=328 K) at the following initial condition:  $P_{SO_2} = 1000$ ,  $P_{NO} = P_{NO_2} = 250$  ppm. The gas to liquid ratio, G/L is 75.
6. The concentration profile of species as a function of reaction time in a batch reactor (pH=5 and temp.=298 K) at the following initial condition:  $P_{SO_2} = 1000$ ,  $P_{NO} = P_{NO_2} = 250$  ppm. The gas to liquid ratio, G/L is 75.



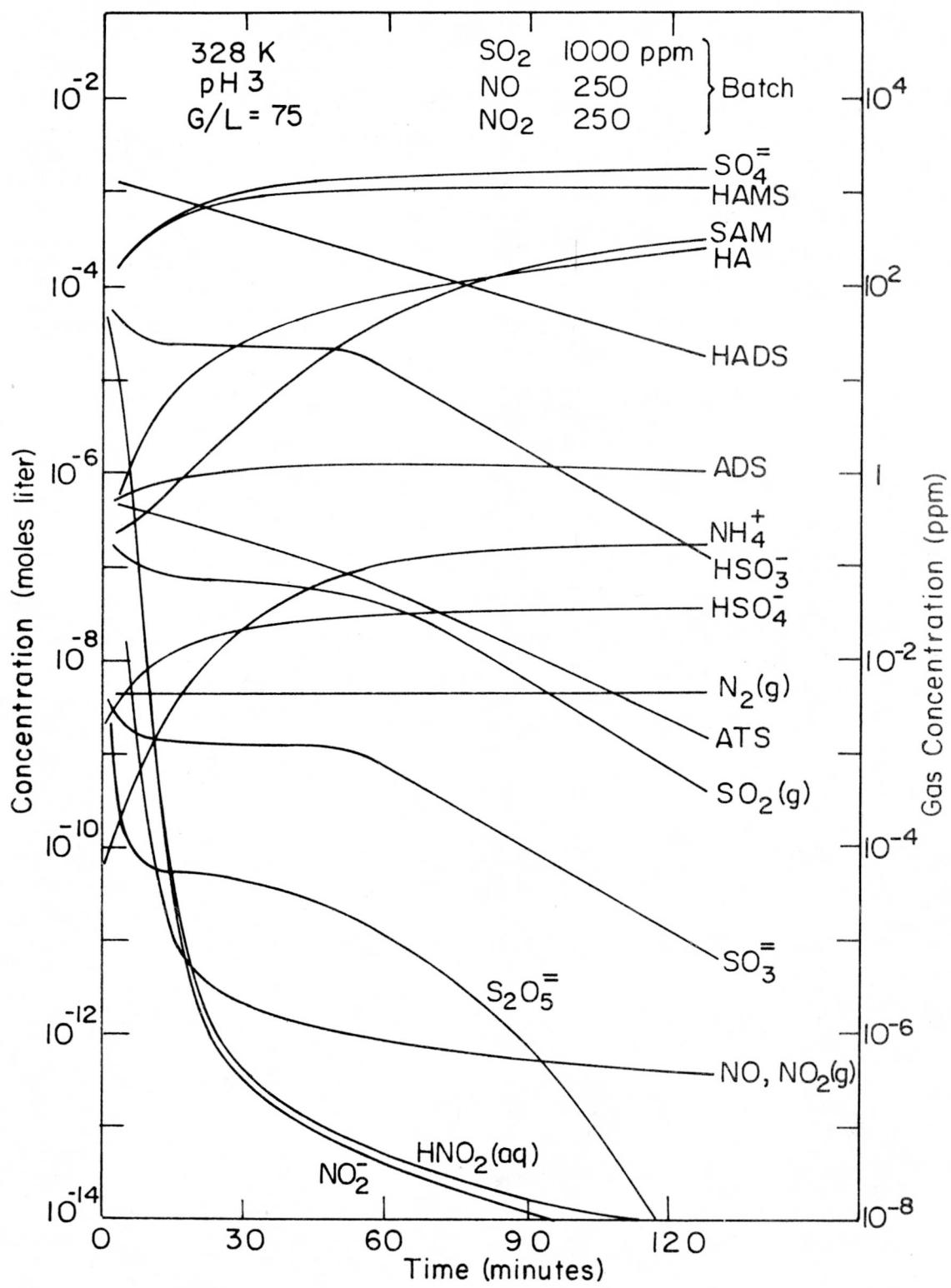
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Figure 1



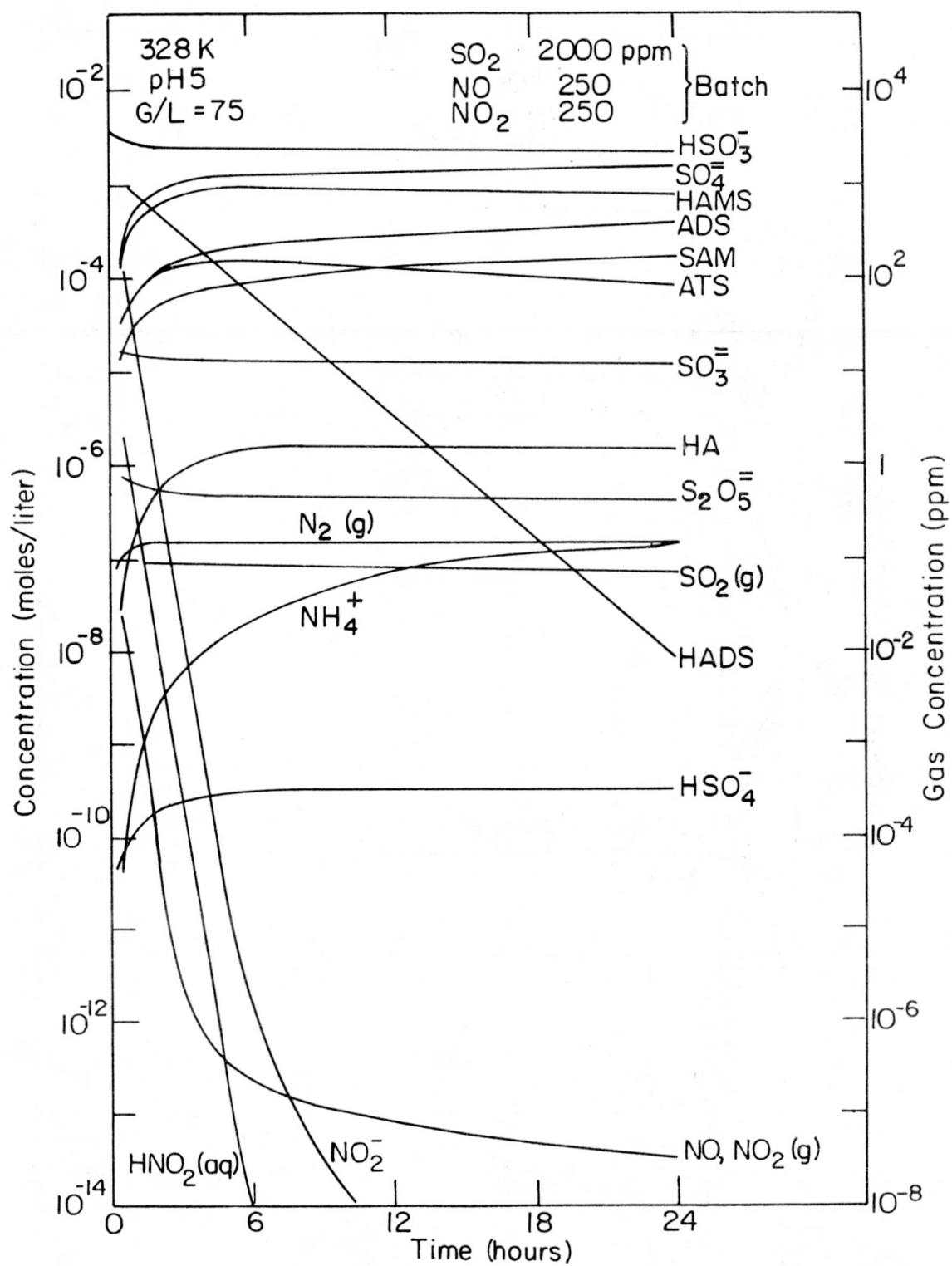
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Figure 2



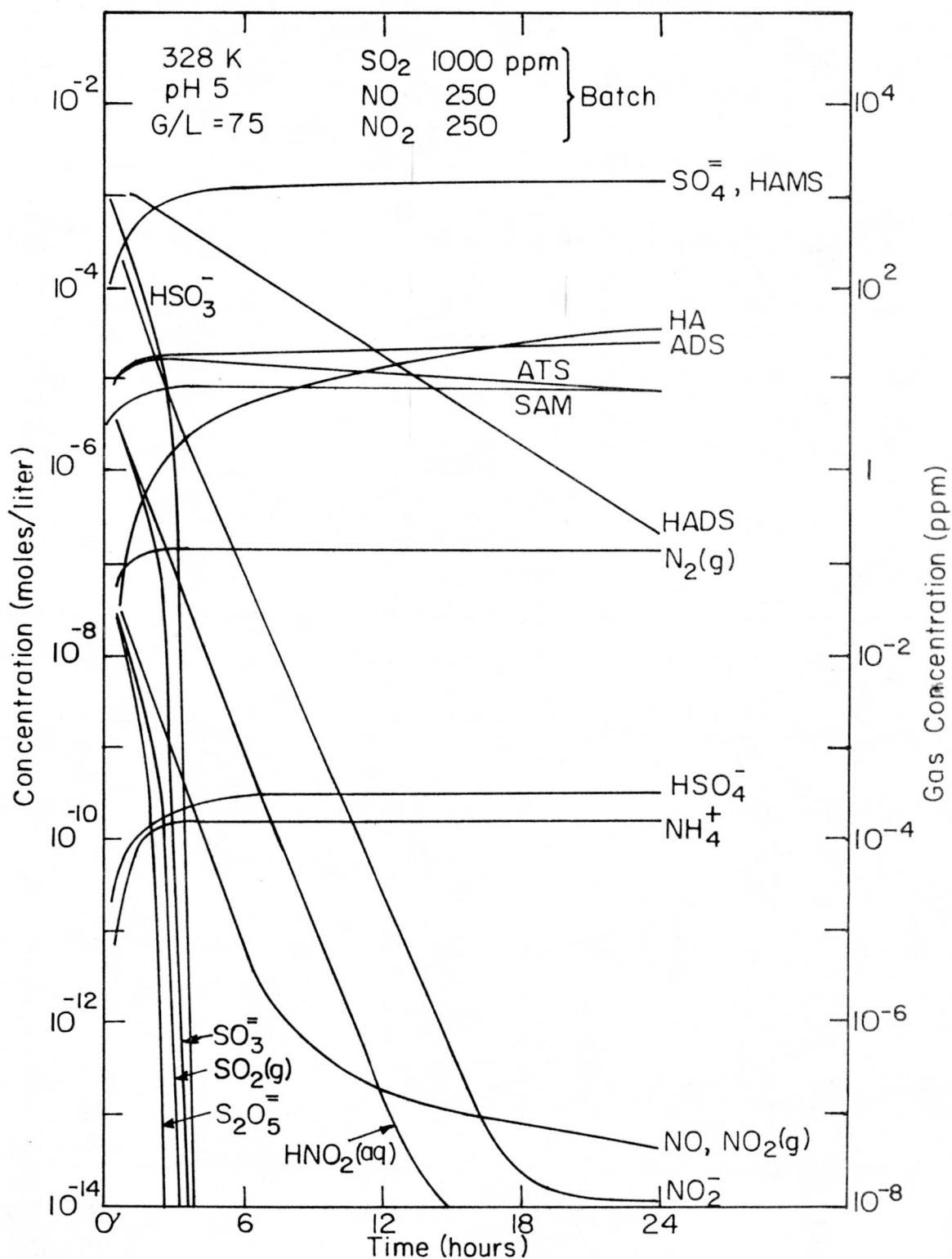
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Figure 3



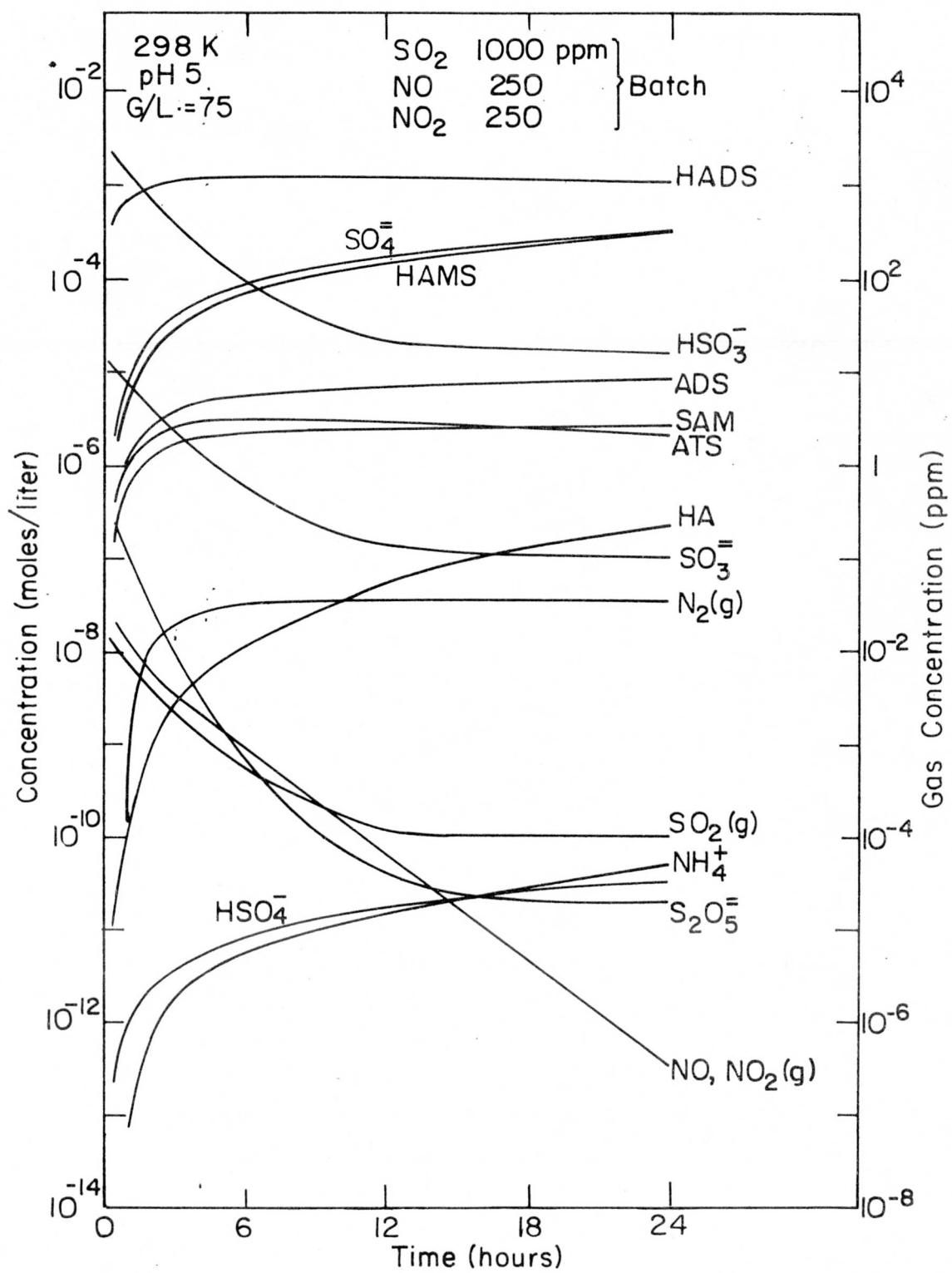
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Figure 4



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Figure 5



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Figure 6

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