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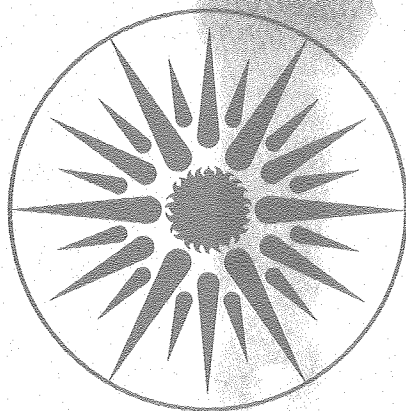
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R. Toossi and T. Novakov

April 1984

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THE LIFETIME OF AEROSOLS IN AMBIENT AIR: CONSIDERATION OF
THE EFFECTS OF SURFACTANTS AND CHEMICAL REACTIONS

By

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Abstract

The relatively long lifetime of droplets in atmospheric haze and fog in comparison with similar droplets of pure water is attributed to the presence of a monolayer of surfactant film and to the accumulation of soluble salts from chemical reactions. The lifetime of these droplets is a significant factor in the evaluation of the role of heterogeneous aqueous chemical reactions occurring in the troposphere. Several mechanisms of SO_2 oxidation in the presence of liquid water are investigated. It is shown that soot-catalyzed oxidation of sulfur dioxide could be responsible for the high level of sulfate concentration observed in the coastal industrial areas.

Introduction

The importance of chemical reactions involving liquid water droplets is well established (Beilke et al, 1978; Hegg and Hobbs, 1978; Middleton et al, 1980). These wet processes are suggested to be important in the formation of atmospheric sulfate and nitrate particulates in clouds and thus contribute to an increase in the acidity of rain. pH levels as low as 2.2 were found in a recent study of Los Angeles fog droplets (LA Times, 9/24/82).

In the past, the assessment of the impact of wet chemical processes has been largely based on the chemical reaction rates. However, when relative humidity is less than unity, droplets evaporate and the reaction rate is limited by the aerosols' evaporation time. Therefore in this paper, the lifetime of these droplets is determined and used to assess the importance of aqueous reactions under atmospheric conditions.

The lifetime of droplets is prolonged at a given relative humidity by the presence of hygroscopic salt nuclei and by surfactant material formed into a film on their surfaces. The presence of insoluble material accentuates this effect by acting as a condensation surface for trace impurities and by increasing the concentration of salt, resulting in a lesser required amount of water for a given size droplet to form. Cloud and fog samples collected by Kuroiwa (1951, 1955) and Ogiwara and Okita (1952) were found to contain soluble and insoluble particles which were similar in nature, form, and size to those produced by haze and combustion. The presence of these impurities in samples of atmospheric liquid water has also been substantiated (Winkler, 1973; Covert et al, 1972).

Several mechanisms believed to be responsible for SO_2 oxidation are considered in this paper, as well as their impact on air quality during episodes involving high concentration of such atmospheric aerosols.

Effects of Impurities on the Rate of Evaporation of Water Droplets

Assuming the evaporation of the droplet proceeds by the effusion of vapors through a boundary layer followed by molecular diffusion into the continuum, the rate of evaporation of a solution droplet can be written as (Fukuta and Walter, 1970):

$$\frac{dr}{dt} = \frac{\rho_{eq}(\infty)}{\rho_l} \frac{S - S_{sat}}{R_I + R_M + R_T} \cdot \frac{1}{r} \quad (1)$$

Where

$$R_I = \frac{1}{v \alpha r}, \quad R_M = \frac{1}{D}, \quad \text{and} \quad R_T = \frac{L^2 \rho_{eq}(\infty)}{K R T^2} \cdot S_{sat}$$

R_I , R_M and R_T are the resistances to free molecular effusion, mass diffusion and heat conduction. S is applied, or bulk, saturation ratio (relative humidity if $S < 1$). S_{sat} is the supersaturation ratio for the solution droplet and is given as:

$$S_{sat} = (1 - \sum_i f_i m_i) \exp\left(\frac{2 \sigma M}{r \rho_l R T}\right) \quad (2)$$

Here, m is the molarity of the solute and f is the pressure lowering factor, which depends on the concentration, temperature, and nature of the solute (International Critical Tables, 1926). The summation is made over all of the ionic species present in the solution. Other parameters are defined in Table 1.

Analytical solutions can be found for limiting cases. For nonpolar liquids and polar liquids with short hydrocarbons, resistance in the interface is negligible ($R_I \approx 0$), and evaporation is controlled by the rate of diffusion of water to the gas phase and conduction of heat to the droplet. With such a droplet that is also large

enough for curvature effects to be neglected, equation (1) can be integrated to give the dimensionless lifetime of the droplet as:

$$\frac{t_d \cdot D}{r_0^2} = \frac{1 + R_T \cdot D}{2 \frac{\rho_{eq}^{(\infty)}}{\rho_l} \cdot (S_{sat} - S)} \quad (3)$$

Polar liquids and droplets containing a monolayer of surfactant film vaporize at significantly lower rates (small value of α), evaporation is kinetically rate-controlled, and $P_I \gg R_M + R_T$ (see Table 2). Under these conditions, equation (1) can be solved to give the lifetime as:

$$\frac{t_k \cdot \nu \cdot \alpha}{r_0} = \frac{1}{\frac{\rho_{eq}^{(\infty)}}{\rho_l} (S_{sat} - S)} \quad (4)$$

In Figure 1, ratios are depicted of the lifetimes of various size droplets calculated using the diffusion model to the lifetimes calculated using equation (1) for various evaporation coefficients. For large droplets and flat surfaces, evaporation is diffusion-controlled. Kinetic effects become important only if the droplet is covered by surfactants of long-chain hydrocarbons with high film resistances. However, the error in using diffusion results can be substantial for atmospheric fog droplets ($r_0 \sim 1-5 \mu\text{m}$) covered with even a relatively weak surfactant.

The effects of relative humidity and temperature upon the lifetime are seen in Figures 2 and 3. At relative humidities of 80% and higher, a stronger correlation between lifetime and humidity can be noted. In regard to the effect of temperature, an exponential increase in lifetime can be observed as temperature decreases. This dependence is primarily due to changes in partial vapor pressure.

Effect of Chemical Reaction

Absorption of gases and chemical reactions within the droplet can eventually reduce the surface vapor pressure to values smaller than equilibrium vapor pressure. Hence, condensation occurs at relative humidities below the saturation limit, causing droplets to grow. The additional layers of water, converging upon the surface of the droplet, facilitate heterogeneous chemical reactions. This results in further droplet growth to sizes which attenuate light and reduce visibility. At the coast line, the higher concentration of salt nuclei shifts the equilibrium droplet size distribution to the larger values. This shift occurs because the critical droplet radius, defined as the radius corresponding to equilibrium at maximum supersaturation, is larger when the aerosol contains salt nuclei. The result is that the probability that the nuclei are wetted is greater at the coast line than in inland areas, allowing more droplets to participate in aqueous chemical reactions.

SO₂ Oxidation in Atmospheric Aqueous Droplets

Sulfur dioxide can be oxidized by photochemical reactions in the gas phase and by catalytic and non-catalytic oxidation in the aqueous droplets. In the humid industrial areas, the rate of sulfate production in the presence of suitable catalysts may sometimes be higher than photo-oxidation by one or more orders of magnitude, (Middleton et al, 1980). Strong oxidizing agents such as ozone (Penkett and Garland, 1974); hydrogen peroxide (Penkett et al, 1976); and metallic ion catalysts such as manganese (Matteson et al, 1969; Johnstone and Moll, 1960); iron (Freiberg, 1972), and copper (Cheng et al, 1971) are cited as possible oxidation pathways in aerosol droplets. Recently, the role of soot particles as catalysts in

SO_2 oxidation reactions has been studied (Brodzinsky et al, 1980). Because of the high concentration of these soot-laden particles in industrial areas, it is plausible that they could be responsible for the production of the major part of sulfate in fogs and clouds and in the formation of acid rain (Chang et al, 1981).

The conditions under which one or all of these oxidation processes are important depend on the meteorological parameters and on the concentration of gaseous species in the atmosphere, as well as on the nature and availability of an oxidizing agent. Liquid water is needed to initiate the reaction, which can be acquired by physical absorption on the surface of an insoluble solid or by hygroscopic soluble salt nuclei in the aerosol.

Whether the rate of SO_2 conversion is controlled by the rate of diffusion of gaseous pollutants toward and within the droplet or by the rate of chemical reactions inside the droplet depends on the size of the droplet, the nature of the gaseous species, and the catalyst involved. Johnstone and Coughanowr (1958) showed that for droplets 700 μm in diameter at saturated humidity, oxidation of SO_2 catalyzed by H_2SO_4 is controlled by the rate of diffusion in the droplet. For droplets smaller than 50 μm in diameter, Beilke and Gravenhorst (1978) showed that the rate-determining step in the overall heterogeneous SO_2 oxidation is the oxidation of S(IV) to sulfate and not a diffusion process. Fog and cloud droplets are usually between 5 and 20 μm ; therefore, it seems safe to assume that the rate of reaction for such droplets in the aqueous phase is the rate-determining step. Under these conditions, the reaction rate depends only on the concentration of the catalyst and on the dissolved species in the solution.

The rate of reaction is independent of droplet size as long as enough water exists on the surface of the catalytic nuclei to sustain the reaction. Small droplets of pure water evaporate long before a measurable amount of sulfate is formed. For larger droplets, evaporation is eventually hindered as the

concentration of dissolved sulfate increases. Steady-state conditions will eventually be maintained, and the droplet will reach a new equilibrium as the reaction goes to completion. In the remainder of this paper, we examine such conditions and assess the importance of several catalytic reactions.

Catalytic Oxidation of SO₂ on Soot Particles

The reaction rate law is shown to be represented by the following equation (Chang et al, 1981):

$$\frac{d[S(VI)]}{dt} = k[C_x][O_2]^{0.69} f[S(IV)] \quad (5)$$

where

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

$[C_x]$ = grams of carbon particles/l

$[O_2]$ = moles of dissolved oxygen/l

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

$\alpha = 1.50 \times 10^{12} \text{ l}^2/\text{mole}^2$

$\beta = 3.06 \times 10^6 \text{ l/mole}$

Strictly speaking, catalytic properties of soot particles are different for various fossil fuels under different combustion conditions. The rate constant used below represents the average value for acetylene and natural gas particles produced under rich flame conditions and is given as:

$$k = 1.17 \times 10^5 \exp(-E/RT) \text{ moles}^{.31} \text{ l}^{.69} / \text{g. sec.}$$

where

T = Temperature in degrees Kelvin, and

$E = 11.7$ kcal/mole

The rate of sulfate production is linearly proportional to $f[S(IV)]$, which decreases as the pH decreases at a given SO_2 concentration. Under atmospheric conditions ($P_{SO_2} = 1-100$ ppb), the rate is drastically reduced when the pH drops to values below 3-4. Using equation (5), the rate of conversion, defined as the fraction of dissolved SO_2 oxidized, is calculated for different values of pH and is plotted in Fig. 4. The conversion rate is initially zeroth order with respect to SO_2 concentration, but the order increases rapidly for smaller SO_2 concentrations and lower pH values.

When the droplet is undergoing evaporation, the following assumptions are made for estimating the rate of conversion:

1. The droplets are independent of each other and their surface temperature remains constant during evaporation.
2. The establishment of equilibrium between SO_2 in the gas phase and $S(IV)$ in the fog droplet is very fast compared to the rate of the chemical reaction.
3. The solubilities of SO_2 and O_2 gases follow Henry's Law.

The rate of evaporation is calculated from equations (1) and (2). The summation is made over all sulfite species ($SO_2 \cdot H_2O$, HSO_3^- , and SO_3^{2-}) and the dissolved salts which might be present. Dissolved gases and the dissociation products are assumed to be in equilibrium with the gaseous vapors. The $[H^+]$ is obtained from charge balance:

$$[H^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}] + [HSO_4^-] + 2[SO_4^{2-}] \quad (6)$$

and the rate of sulfate formation ($[\text{HSO}_4^-] + [\text{SO}_4^{=}]$) is given by equation (5). The chemical equilibrium constants used are listed in Table 3. Differential equations (1) and (5), given the set of equilibrium relations in Table 3, are solved simultaneously to determine the size and acidity of the droplet at different times. Figure 5 shows such results for a fog droplet $5\mu\text{m}$ in radius when it evaporates and undergoes catalytic reactions in the atmosphere at a relative humidity of 80%. A carbon concentration of $10\text{ }\mu\text{g}/\text{m}^3$ is taken as a typical value for urban areas, assuming that elemental carbon constitutes 30% of the total weight. An evaporation coefficient of $\alpha = 10^{-4}$ was assumed, having been measured experimentally for ambient aerosols by Toossi et al (1980).

In reviewing Figure 5 it can be seen, under the given assumptions, that the droplet of pure water evaporates completely in less than one second (Curve a). The equilibrium radius ($.07\text{ }\mu\text{m}$) is too small for any wet reaction to take place. The carbon nuclei present in such a droplet will possibly dry out. The rate of reaction will then follow the dry mechanism, which has a reaction rate slower than that of the wet mechanism by at least two orders of magnitude. Thus, it appears that carbon-catalyzed SO_2 oxidation is not an important mechanism in regions of lower relative humidity.

In coastal areas concentration of salt nuclei is higher, causing the equilibrium radius of an aerosol droplet to be larger, the lower vapor pressure associated with surfactants and other impurities help to maintain the liquid water required for the wet reaction. Curve b represents the evaporation of an aerosol containing such impurities. When the aerosol contains carbonaceous materials, chemical reactions also play an important role. In this case, gaseous pollutants absorbed in the aerosols produce sulfite and bisulfite ionic species which are then oxidized to sulfate. As evaporation proceeds, aerosol is being rapidly concentrated and the solution effects become more pronounced. Eventually, the vapor pressure at

the surface falls below that of the surrounding atmosphere. Evaporation is hindered completely and the aerosol starts to grow. The rate of growth, however, slows down as pH becomes reduced. Under such conditions as discussed above, pH levels of 2.5 or lower may be achieved in less than an hour, (see Curve c, Fig. 5). The lifetimes of these droplets are limited by their rates of fall and not by evaporation, as is the case for pure droplets.

This procedure has been repeated for different initial conditions and the results are summarized in Table 4. Below, are summarized some generalizations which can be made regarding this table:

- i. Concentration of salt nuclei and other impurities only affect the equilibrium radius. Percent conversion is independent of these parameters when sufficient water for the aqueous reaction is available.
- ii. Increasing the concentration of soot particles increases the rate of conversion initially. However, as the reaction proceeds, pH drops and the reaction becomes less effective. The result is only a moderate increase in the total rate of conversion.
- iii. When the NH_3 concentration in the atmosphere becomes reduced, the ammonia concentration in solution lessens. The ammonia acts as a buffer, thereby decreasing the solution acidity. The effect of NH_3 concentration can, therefore, be studied by observing the oxidation rate at different pH levels.
- iv. The conversion rate is strongly dependent upon the SO_2 partial pressures. Nevertheless, the total amount of sulfate produced is only slightly affected by the SO_2 concentration in the ambient.
- v. Larger aerosols are seen to be less efficient in SO_2 conversion. This is due to the fact that larger droplets evaporate at a much slower rate, causing the concentration of soot particles to remain small throughout the

evaporation. At the limit, where no evaporation exists, Fig. 4, can be used to directly evaluate the rate of conversion.

Comparison with Other Mechanisms

The relative importance of sulfate production mechanisms by soot particles with other mechanisms involving liquid water is investigated by using a box-type model. Details regarding such investigations are reported elsewhere (Chang et al, 1981). The calculations are made for concentrations of gaseous and particulate emission which are usually observed at atmospheric conditions. The results are shown in Figure 6.

It is seen from Fig. 6 that oxidation reactions involving soot particles can comprise the dominant mechanism in fog and cloud droplets and in regions close to sources and heavily polluted urban areas. It should be noted that under conditions of strong photochemical activity, liquid-phase oxidation of SO_2 by H_2O_2 and condensation of H_2SO_4 are two mechanisms likely to be dominant and must be included in any sulfate production mechanisms study.

Conclusions

In this paper, we discussed the rate of soluble and insoluble matter in the stabilization of aerosol droplets. Soluble nuclei, much like sea salt, determine the equilibrium size of the droplet in relation to the surrounding atmosphere. If the nuclei are large enough to wet the aerosol, the absorption of gases followed by chemical reactions in the liquid phase instigates growth of the particle. Different reaction pathways on the oxidation of SO_2 in ambient aerosols have been investigated. The study has been only a limited one. In order to assess the prevalent reaction mechanism, other factors, such as primary source input and meteorological parameters, as well as removal, transport and mixing parameters, must

be included. Also, studies to determine the activity coefficients of different ionic species present in the droplet under concentrated conditions are crucial for a better understanding of this phenomenon.

Acknowledgments

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Table 1

Nomenclature

α	Evaporation coefficient
k	Thermal conductivity of the medium
v	Velocity of the evaporating molecule
ρ	Density
σ	Surface tension
D	Diffusion coefficient
f	Pressure lowering factor
L	Latent heat of evaporation
m	molarity
M	Molecular weight
r	Droplet radius
$\overline{R}$	Universal gas constant
S	Relative humidity, saturation ratio
t	Time
T	Droplet temperature

Subscripts

eq	Equilibrium
l	Liquid
s	Solid
∞	Medium

Table 2
Resistances for Different Droplet Sizes at $T = 20^\circ\text{C}^*$

$r(\mu\text{m})$	$R_m (\text{sec.cm}^{-2})$	$R_T (\text{sec.cm}^{-2})$	$R_i (\text{sec. cm}^{-2})$		
			$\alpha = 10^{-2}$	$\alpha = 10^{-4}$	$\alpha = 10^{-6}$
0.1	3.9	10	7×10^2	7×10^4	7×10^6
1	3.9	10	7×10^1	7×10^3	7×10^5
10	3.9	10	7	7×10^2	7×10^4
100	3.9	10	7×10^{-1}	7×10^1	7×10^3
1000	3.9	10	7×10^{-2}	7	7×10^2

* The thermal conductivity and diffusion coefficient are approximated by the empirical relations:

$$K(T) = 5.803 \times 10^{-5} \left(\frac{393}{T + 120} \right) \left(\frac{T}{273} \right)^{3/2} \frac{\text{cal}}{\text{cm} \cdot \text{sec} \cdot ^\circ\text{K}}$$

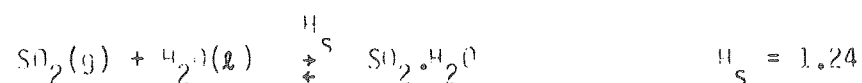
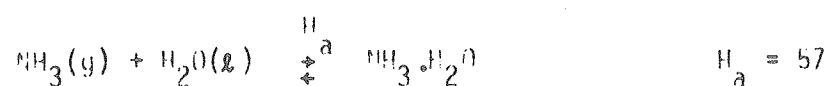
$$D(T) = 0.226 \left(\frac{393}{T + 120} \right) \left(\frac{T}{273} \right)^{5/2} \cdot \frac{1}{p} \text{ cm}^2/\text{sec}$$

The latent heat of evaporation is also a function of temperature and can be approximated by the equation,

$$L = - 0.57 T + 753.1 \text{ (L in cal/g and T in } ^\circ\text{K)}$$

between temperature range of interest, $253 < T < 313$. The value of $\sigma = 75 \text{ dynes/cm}$ and $\rho_l = 1 \text{ gm/cm}^3$ is assumed for water.

Table 3
Chemical Equilibrium Constants at 25°C.*



*Concentration in mol l^{-1} and gas pressure in atm. Values obtained from the following data sources: McKay (1971) for K_2 , H_a , K_a , H_s , K_{1s} , K_{2s} ; Handbook of Chemistry and Physics (1961) for K_{3s} .

Table 4
Effect of Variation of Selected Parameters upon the Rate of Conversion

S	R ₀ (μ m)	α	Salt (g)	Soot (μ g/cm ³)	SO ₂ (ppb)	NH ₃ (ppb)	pH	τ	After 1 hr	
									pH	%Conv
.8	5	10 ⁻⁶	10 ⁻¹⁴	10	50	0	4.5	3.27	2.30	8.2
.8	5	10 ⁻⁶	10 ⁻¹³	10	50	0	4.5	3.32	2.32	8.2
.8	5	10 ⁻⁵	0	10	50	0	4.5	.43	1.60	3.2
.8	5	10 ⁻⁴	0	10	50	0	4.5	*	--	--
.8	5	10 ⁻⁶	0	10	50	0	4.5	3.22	2.10	8.2
.8	5	10 ⁻⁶	0	100	50	0	4.5	3.30	2.26	9.5
.8	5	10 ⁻⁶	0	10	5	0	4.5	3.20	3.00	6.0
.8	5	10 ⁻⁶	0	10	500	0	4.5	3.26	2.79	1.1
.8	5	10 ⁻⁶	0	10	50	5	5.8	3.27	2.37	8.2
.8	5	10 ⁻⁶	0	10	50	50	6.3	3.27	2.56	8.2
.8	5	10 ⁻⁶	0	10	50	500	6.7	3.27	3.83	8.3
.8	50	10 ⁻⁶	0	10	50	0	4.5	31.2	3.20	1.2
.8	500	10 ⁻⁶	0	10	50	0	4.5	498	4.30	1.2

*Droplet evaporates after 99.6 seconds.

Figure 1. The dimensionless lifetime of a droplet covered with a film of surfactant. t_d is lifetime at limiting case when evaporation is diffusion controlled. t_ℓ is calculated lifetime when both diffusion and kinetic effects are considered. This graph shows the range of validity of the diffusion model.

Figure 2. The effect of relative humidity on the lifetime of a droplet at 20°C.

Figure 3. The lifetime of droplets as a function of temperature ($S = .8$).

Figure 4. Rate of conversion of SO_2 to sulfate at various pH levels and SO_2 concentration.

Figure 5 The radius of an evaporating aerosol droplet in which oxidation reaction ($\text{SO}_2 \xrightleftharpoons[C_x]{\text{O}_2} \text{SO}_4^{2-}$) occurs.

$T = 10^\circ\text{C}$, $S = .8$, $r_0 = 5 \text{ m}$, $P_{\text{SO}_2} = 100 \text{ ppb}$, $P_{\text{NH}_3} = 5 \text{ ppb}$,
 $\alpha = 10^{-4}$, and $C_x = 10 \text{ } \mu\text{g/m}^3$, $m_{\text{NaCl}} = 10^{-13} \text{ gr}$

.... Pure water droplet $\alpha \rightarrow \infty$ (no catalyst, no chemical reaction)

---- Droplet containing soluble salt nuclei.

_____ Droplet containing soluble salt nuclei and insoluble carbon catalyst, covered by a film of surfactant with $\alpha = 10^{-4}$

Figure 6 Comparison of the relative importance of various sulfate production mechanisms involving liquid water based on a box-type calculation. The following initial conditions were used in the calculation:

$P_{\text{SO}_2} = 0.01 \text{ ppm}$, $P_{\text{CO}_2} = 0.000311 \text{ atm}$; $P_{\text{NH}_3} = 5 \text{ ppb}$; $P_{\text{O}_3} = 0.05 \text{ ppm}$;
 $P_{\text{HNO}_2} = 8 \text{ ppb}$; $[\text{Fe}^{+3}] = 1.2 \times 10^{-7} \text{ mol l}^{-1}$; $[\text{Mn}^{+2}] = 1.8 \times 10^{-8} \text{ mol l}^{-1}$;
 $\text{soot} = 10 \text{ } \mu\text{g m}^{-3}$; and liquid water = 0.05 gm^{-3} .

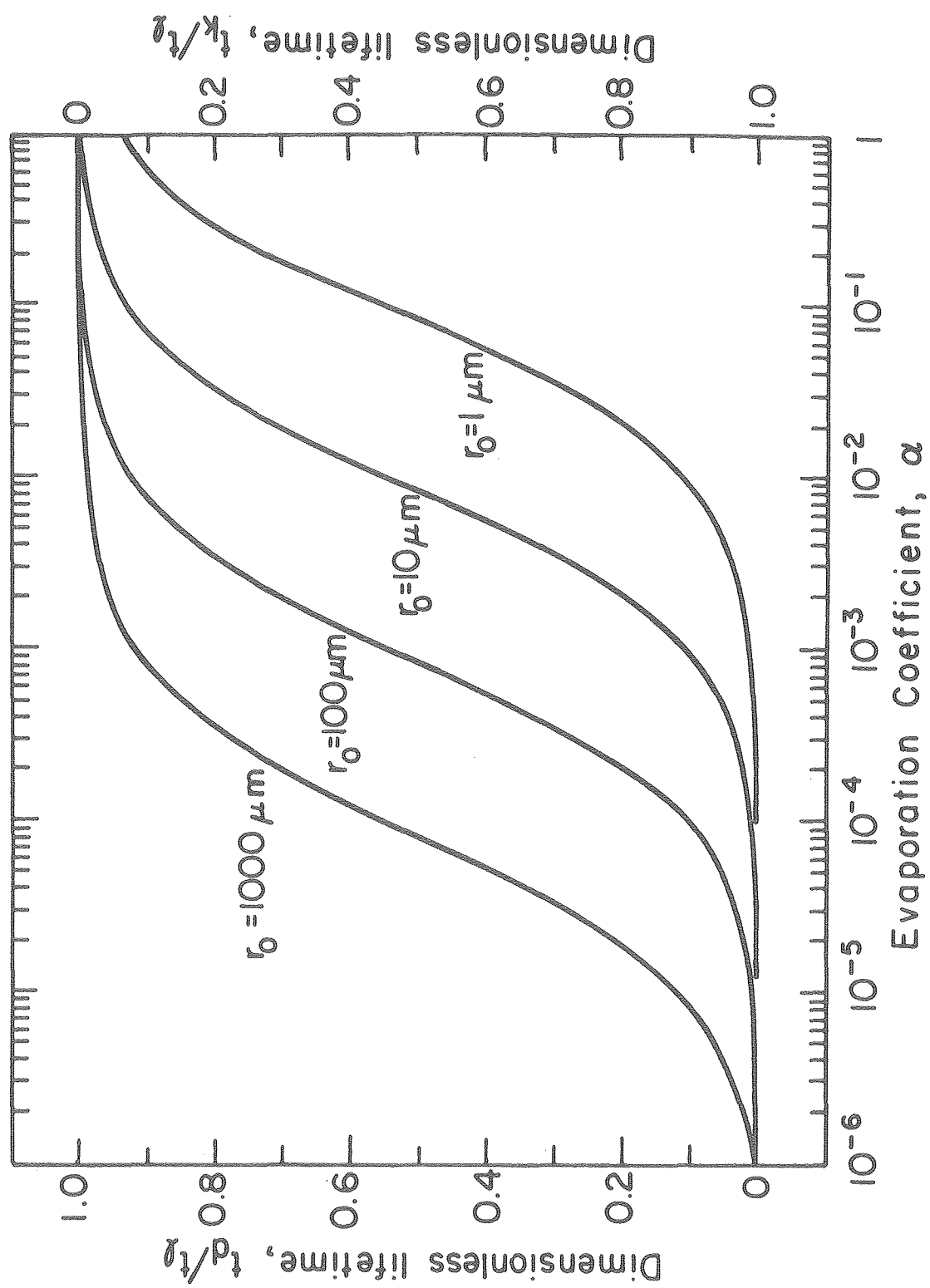


figure 1

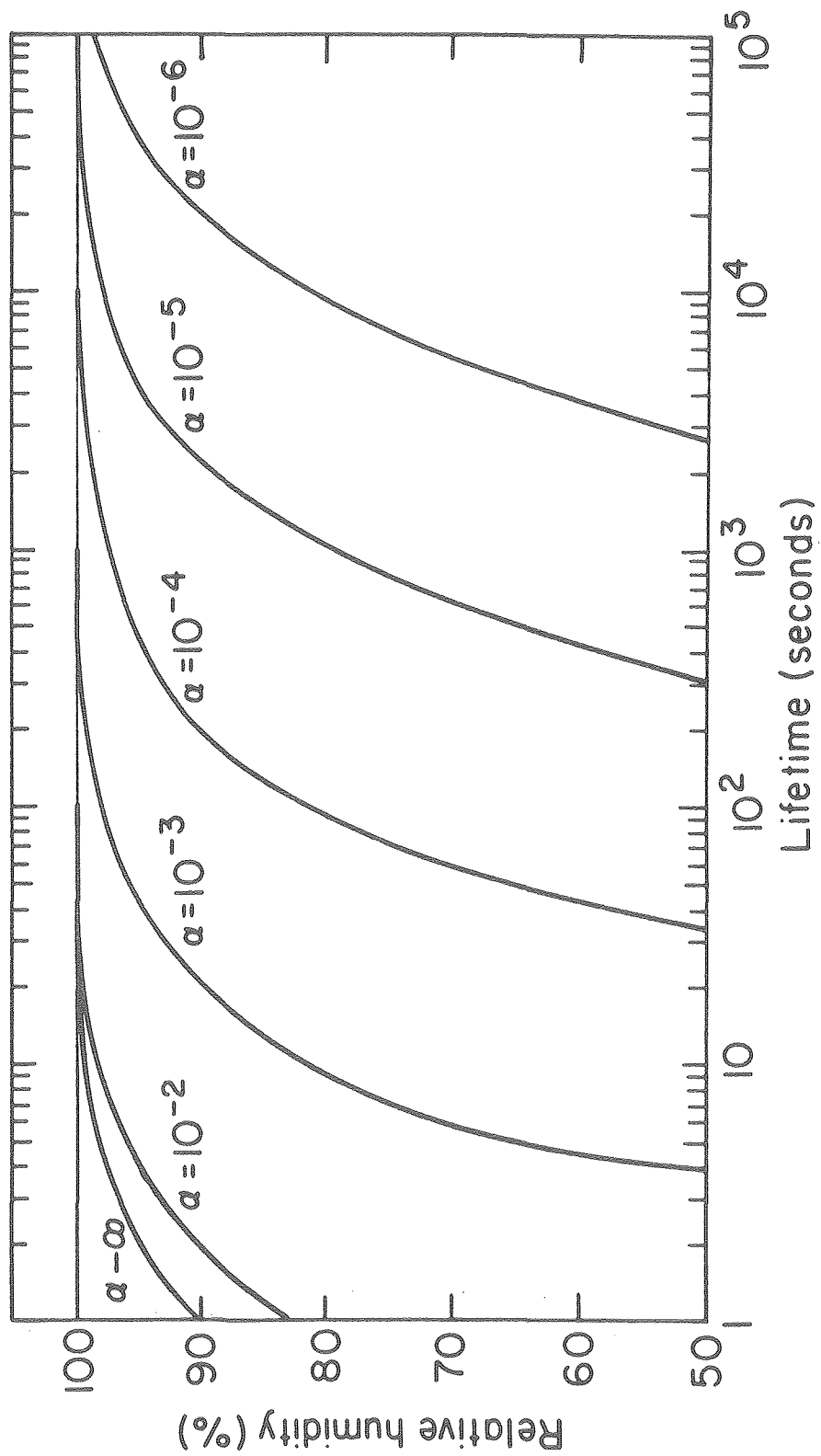


figure 2

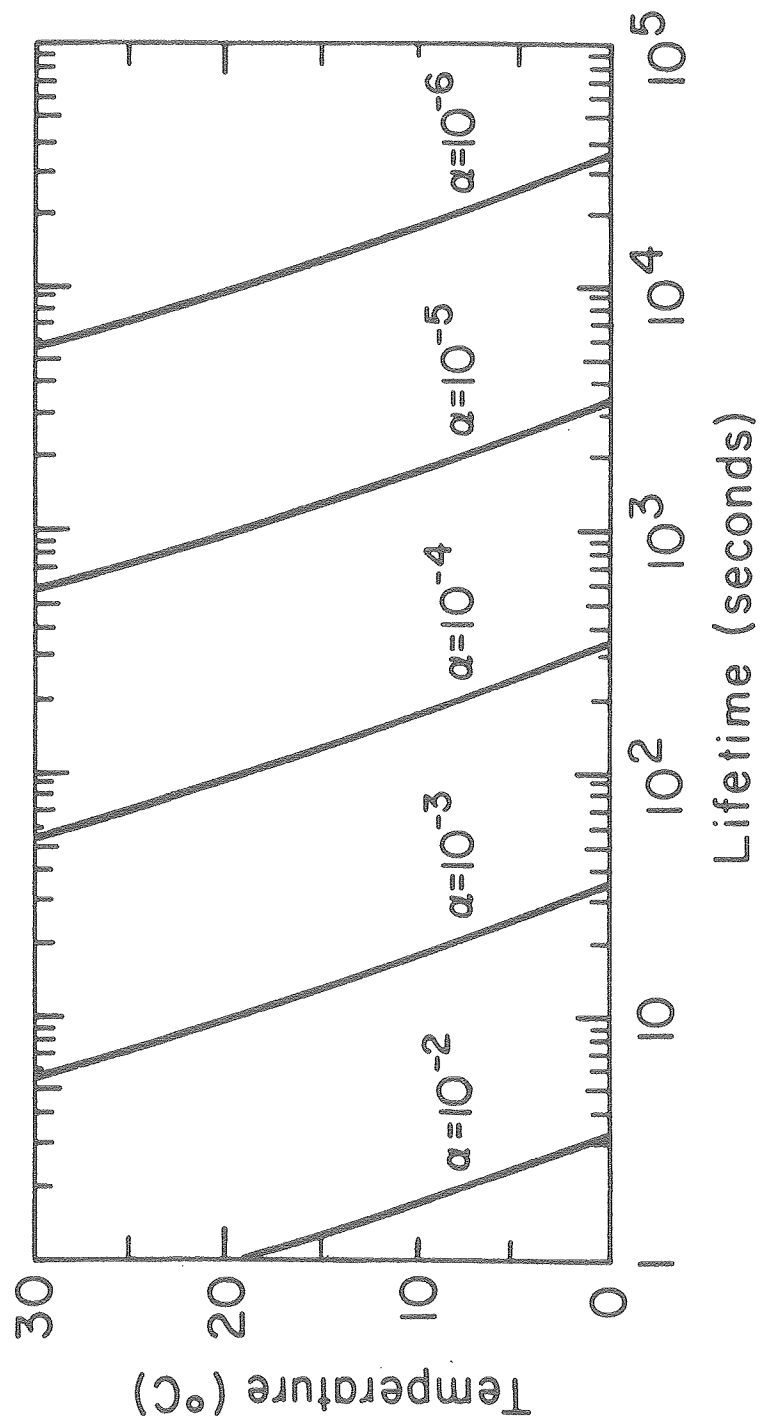


figure 3

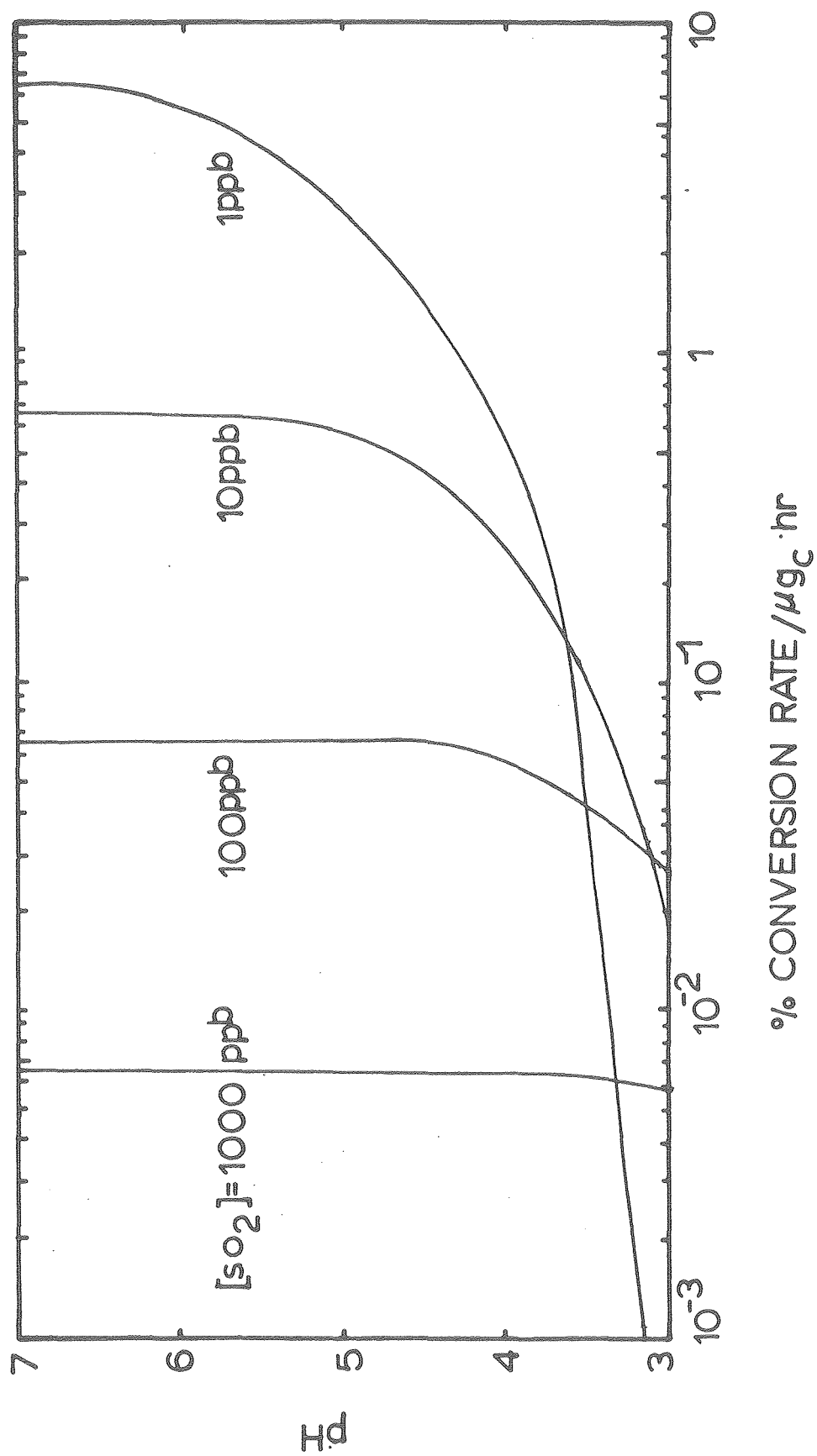


figure 4

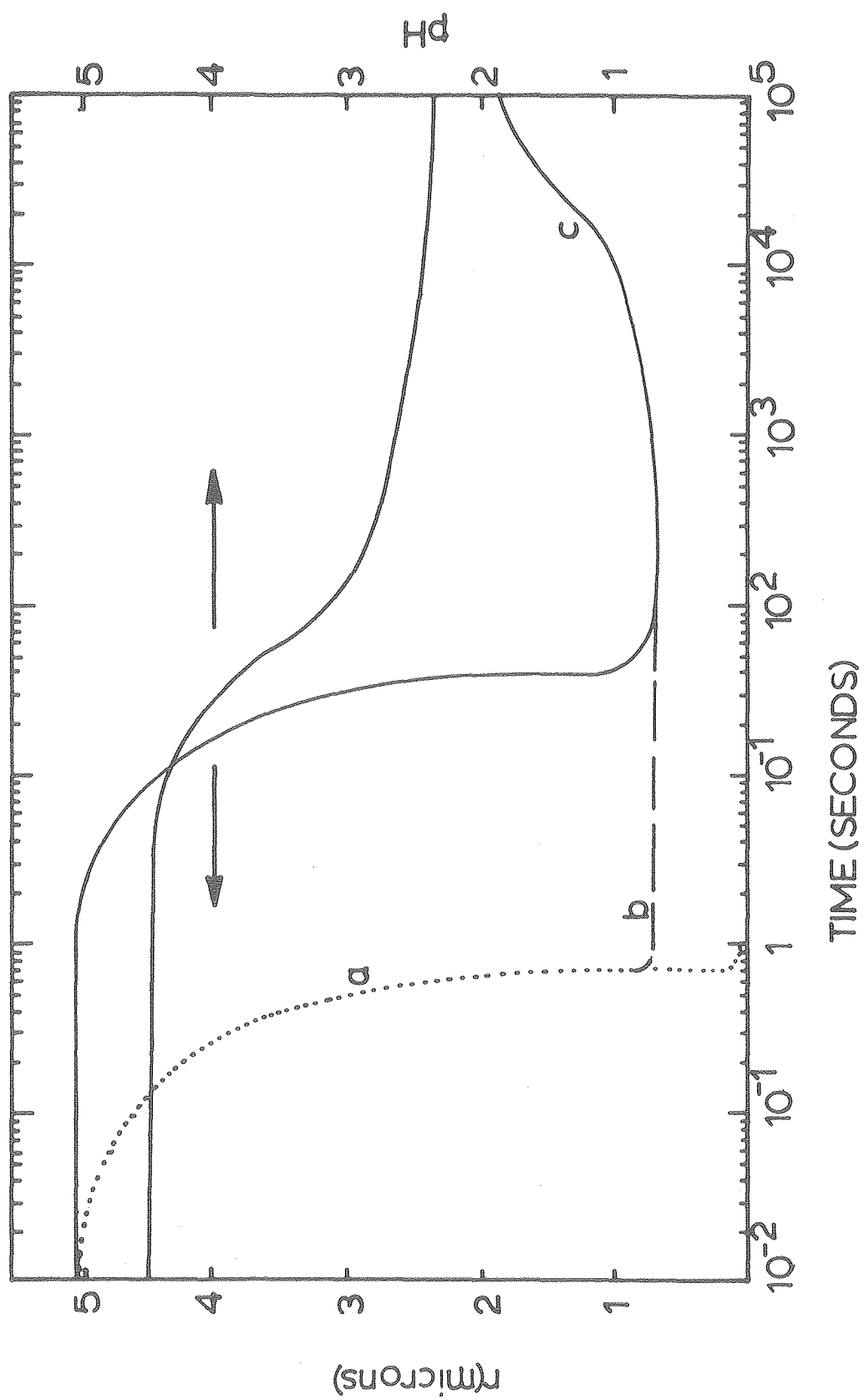


figure 5

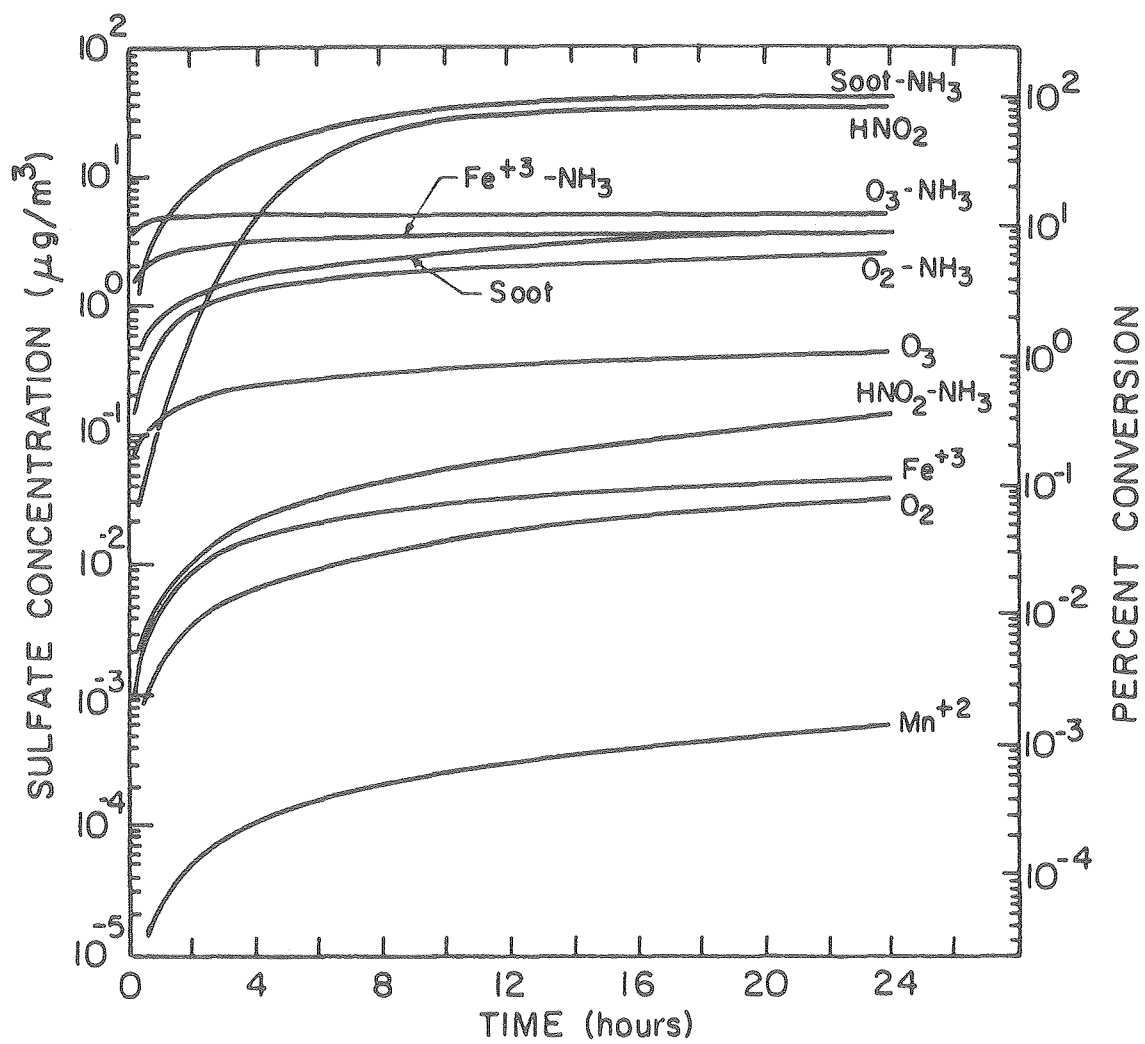


figure 6