Chemistry of a polluted cloudy boundary layer

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Chemistry of a Polluted Cloudy Boundary Layer

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A one-dimensional photochemical model for cloud-topped boundary layers is developed which includes detailed descriptions of gas-phase and aqueous-phase chemistry, and of the radiation field in and below cloud. The model is used to interpret the accumulation of pollutants observed over Bakersfield, California, during a wintertime stagnation episode with low stratus. The main features of the observations are well simulated; in particular, sulfate accumulates progressively over the course of the episode due to sustained aqueous-phase oxidation of SO$_2$ in the stratus cloud. The major source of sulfate is the reaction S(IV) + Fe(III), provided that this reaction proceeds by a non radical mechanism in which Fe(III) is not reduced. A radical mechanism with SO$_2$ and Fe(II) as immediate products would quench sulfate production because of depletion of Fe(III). The model results suggest that the non radical mechanism is more consistent with observations, although this result follows from the absence of a rapid Fe(II) oxidation pathway in the model. Even with the non-radical mechanism, most of the soluble iron is present as Fe(II) because Fe(IIID) is rapidly reduced by O$_2$. The S(IV) + Fe(III) reaction provides the principal source of H$_2$O$_2$ in the model; photochemical production of H$_2$O$_2$ from HO$_2$ or O$_2$(1) is slow because HO$_2$ is depleted by high levels of NO$_3$.

The aqueous-phase reaction S(IV) + OH initiates a radical-assisted S(IV) oxidation chain but we find that the chain is not propagated due to efficient termination by SO$_4^-$ + Cl$^-$ followed by Cl + H$_2$O. A major uncertainty attached to that result is that the reactivities of S(IV)-carbonyl adducts with radical oxidants are unknown. The chain could be efficiently propagated, with high sulfate yields, if the S(IV)-carbonyl adducts were involved in chain propagation. A remarkable feature of the observations, which is well reproduced by the model, is the close balance between total atmospheric concentrations of acids and bases. We argue that this balance reflects the control of sulfate production by NH$_3$, which follows from the pK dependence of the S(IV) + Fe(III) reaction. Such a balance should be a general characteristic of polluted environments where aqueous-phase oxidation of SO$_2$ is the main source of acidity. At night, the acidity of the cloud approaches a steady state between NH$_3$ emissions and H$_2$SO$_4$ production by the S(IV) + Fe(III) reaction. A steady state analysis suggests that [H$^+$] at night should be proportional to (E$_{SO_2}$/E$_{NH_3}$)$^{1/2}$, where E$_{SO_2}$ and E$_{NH_3}$ are emission rates of SO$_2$ and NH$_3$, respectively. From this analysis it appears that cloud water pH values below 3 are unlikely to occur in the Bakersfield atmosphere during the nighttime hours. Very high acidities could, however, be achieved in the daytime because of photochemical acid production by the gas-phase reactions NO$_3$ + OH and SO$_2$ + OH.

I. INTRODUCTION

This paper describes an attempt to simulate the chemical evolution of the atmosphere over Bakersfield, California, during an extended wintertime stagnation episode with low stratus. We focus our attention on the oxidation of SO$_2$ to sulfate, and on the concomitant production of acidity. The city of Bakersfield experiences severe sulfate pollution in winter; sulfate aerosol concentrations as high as 1600 neq m$^{-3}$ (24-hour average) have been measured [Duckworth and Crowe, 1979]. Bakersfield is located at the southern end of the San Joaquin Valley, in a region of major oil recovery operations which emit large amounts of SO$_2$. The ventilation of the San Joaquin Valley is often restricted in the wintertime because of a strong subsidence inversion based a few hundred meters above the valley floor. Such high-inversion stagnation episodes can persist uninterrupted for a week or more and are usually accompanied by extensive fog or stratus [Holts and Swanson, 1981].

The restricted ventilation and the presence of large amounts of suspended liquid water provide favorable conditions for observing the oxidation of locally emitted SO$_2$ to sulfate. Jacob et al. [1986] (hereafter referred to as JMWH) made extensive measurements of aerosol composition at a network of sites in the San Joaquin Valley during a stagnation episode which lasted from January 3 to 7, 1984. They observed a progressive accumulation of sulfate aerosol over the period January 3-5 when the valley was capped by a persistent stratus deck. Sulfate concentrations decreased on January 6 following widespread fog, presumably because of fog deposition [Waldman et al., 1987]. Throughout the episode, a close balance was observed between high atmospheric concentrations of acids (mainly H$_2$SO$_4$ and HNO$_3$) and bases (mainly NH$_3$). This balance was found to be a general characteristic of stagnation episodes in the southern San Joaquin Valley [Munger et al., 1983; Jacob et al., 1984].

We will address in this paper two major questions raised by the Bakersfield data of JMWH: (1) What were the mechanisms of sulfate production? (2) Why did the concentrations of acids and bases remain in close balance at all times?

There is considerable evidence that oxidation of SO$_2$ to sulfate is enhanced in cloud compared to clear air due to aqueous-phase reactions of dissolved SO$_2$. Aqueous-phase oxidation of SO$_2$ by H$_2$O$_2$ is particularly rapid; Daum et al. [1984] observed that H$_2$O$_2$ and SO$_2$ are mutually exclusive in clouds, suggesting rapid titration. Tropospheric concentrations of H$_2$O$_2$ are of the order of 1 ppb [Logan et al., 1981; Heikes et al., 1987]. In polluted environments such as Bakersfield the concentrations of SO$_2$ are usually

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TABLE 1. Nomenclature of species

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<th>Species</th>
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<tr>
<td>S(VI)</td>
<td>H$_2$SO$_4$(aq) + HSO$_4^-$ + SO$_4^{2-}$ + FeSO$_4^2$</td>
</tr>
<tr>
<td>S(IV)</td>
<td>SO$_4^{2-}$(aq) + HSO$_4^-$ + SO$_4^{2-}$ + FeSO$_4^2$ + HMS + HAMS + GMBS + (2x)GDBS</td>
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<tr>
<td>N(V)</td>
<td>HNO$_3$(g) + HNO$_3$(aq) + NO$_3^-$</td>
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<tr>
<td>N(-III)</td>
<td>NH$_3$(g) + NH$_3$(aq) + NH$_4^+$</td>
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<td>Fe(II)</td>
<td>Fe$^{2+}$ + Fe(OH)$_2$</td>
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<tr>
<td>Fe(III)$_{aq}$</td>
<td>Fe$^{3+}$ + Fe(OH)$_2$ + Fe(OH)$_3$ + FeSO$_4^2$ + FeHOSO$_3$ + FeSO$_4^2$</td>
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<td>Fe(III)$_{aq}$ + Fe(OH)$_3$</td>
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<td>O$_2$(aq) + O$_2^-$</td>
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<td>GLYXA</td>
<td>CHOCHO(aq) + CHOCHOH(OH)$_2$ + CH(OH)$_2$CH(OH)$_2$</td>
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<td>MGLYX</td>
<td>CH$_3$COCHO(aq) + CH$_3$COCHOH(OH)$_2$</td>
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<td>HMS</td>
<td>H$_2$C(OH)SO$_3^-$</td>
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<td>HAMS</td>
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<td>GDBS</td>
<td>CH(OH)SO$_3^2$ CH(OH)SO$_3$</td>
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much higher, so that the oxidation of SO$_2$ by H$_2$O$_2$ is limited by the rate of H$_2$O$_2$ production. Chameides and Davis [1982] suggested that vigorous H$_2$O$_2$ production could take place in cloud droplets by the aqueous-phase reaction H$_2$O + O$_2$ in the boundary layer [Gervat et al., 1988], but this source should be small in our case since the residence time of air in the Joaquin Valley during stagnation episodes is on the order of several days [Reible, 1982; JMWH]. The fact that SO$_2$ oxidation was observed in the JMWH study suggests either that SO$_2$ oxidants other than H$_2$O$_2$ dominated sulfate production or that H$_2$O$_2$ was produced rapidly by a mechanism not recognized in previous chemical models.

We will show in this paper that the Fe(III)-catalyzed autoxidation of S(IV) can explain most of the sulfate production observed in the JMWH study, as well as the close balance between acids and bases. The importance of transition metal ions as aqueous-phase SO$_2$ oxidants in polluted environments has been hypothesized in several model papers [Jacob and Hoffmann, 1983; Seigneur and Saxena, 1984; Graedel et al., 1986]. Jacob and Hoffmann [1983] argued that the Fe(III)- and Mn(II)-catalyzed autoxidation of S(IV) could provide the major source of sulfate in urban nighttime fogs. Recent kinetic work suggests that these processes may be even more important than previously calculated in the models. Martin and Hill [1987a,b] found that the rate constants previously reported for the S(IV) + Fe(III) and S(IV) + Mn(II) reactions underestimate several times the values to be expected in clouds because of the strong dependence of the rate constant on ionic strength. Conklin and Hoffmann [1988a] proposed a non-radical mechanism for the S(IV) + Fe(III) reaction in which Fe(III) acts as a catalyst for the autoxidation of S(IV); this mechanism yields H$_2$O$_2$ as a reaction product, effectively doubling the yield of sulfate. However, Martin [1988] argued that the S(IV) + Fe(III) reaction proceeds by a radical mechanism with Fe(II) and SO$_3$ as immediate products. We will see that the choice of mechanism has a major effect on the predicted sulfate concentrations.

Another significant source of sulfate is the oxidation of SO$_2$ by OH, both in the gas phase and in the aqueous phase. The aqueous-phase reaction S(IV) + OH produces SO$_3$ and initiates a S(IV) oxidation chain propagated by oxidation of SO$_3$ to SO$_2$ and reactions of the successive radical intermediates SO$_3$ and C$_2$H$_4$ with S(IV) [McElroy, 1986b]. Recent kinetic studies have increased considerably our understanding of the propagation reactions involving HSO$_3^-$ and SO$_3^-$ as the reactive S(IV) species [Huie and Neta, 1984, 1987; McElroy, 1988; Wine et al., 1989]. However, in polluted clouds, S(IV) is mainly present as S(IV)-carbonyl adducts [Munger et al., 1986], whose reactivities with the above radicals are unknown. The importance of the aqueous-phase reaction S(IV) + OH as an atmospheric source of sulfate depends in a crucial measure on the participation of S(IV)-carbonyl adducts in the chain initiation, propagation, and termination steps. The main features of this dependence will be outlined here.

Our discussion will be based on a one-dimensional photochemical model which includes comprehensive descriptions of gas-phase and aqueous-phase chemical processes, and detailed computation of radiation intensities in and below cloud. The model is used to simulate the chemical evolution of the atmosphere over Bakersfield during the January 3-5, 1984, stagnation episode documented by JMWH. Throughout that episode the boundary layer was capped by a strong inversion based at approximately 400 m above ground level (AGL), and a nonprecipitating stratus cloud occupied the upper part of the boundary layer below the inversion. We describe the model in section 2 (the solution to the equation of radiative transfer for the cloudy atmosphere is presented in the appendices). Section 3 gives an overview of model results focusing on comparisons with observations. The different aqueous-phase S(IV) oxidation mechanisms contributing to sulfate production are analyzed in section 4. Sensitivity calculations are discussed in section 5 and demonstrate that sulfate production in the model is controlled by the availability of NH$_3$, thus explaining the close
balance observed in the field between total concentrations of acids and bases. The sensitivity of cloud water pH to changes in emissions is discussed in light of this result. Concluding remarks are in section 6.

2. Model Description

The transport of pollutants is simulated with a one-dimensional dynamical model for the cloud-topped boundary layer. Gas-phase chemistry is modeled with the detailed photochemical smog mechanism of Lurmann et al. [1986], and aqueous-phase chemistry is modeled with an updated version of the Jacob [1986] mechanism. The radiation intensities in and below cloud are computed by solution to the equation of radiative transfer for a Mie-scattering plane-parallel atmosphere. Computation of gas-droplet transfer fluxes accounts for gas-phase, interfacial, and aqueous-phase resistances to mass transport [Schwartz and Freierberg, 1981; Jacob, 1986]. In this section we discuss the original and case-specific components of the model. Detailed discussions of the gas-phase chemistry and gas-droplet transfer components can be found in the original references.

Many chemical species of importance to the simulation are rapidly exchanged between the gas phase, the cloud droplets, and the below-cloud aerosol. To facilitate the presentation we make extensive use of a nomenclature based on oxidation states (Table 1). The nomenclature also includes abbreviations for some of the organic aqueous-phase species. We define $[A]$ as the concentration of constituent $A$ per unit volume of cloud water, and $(A)$ as the concentration of $A$ per unit volume of air. Cloud water concentrations are given in units of $M$ (moles per liter of water), aerosol concentrations in units of $m^3$ or $cm^3$ (moles or equivalents per cubic meter of air), and gas-phase concentrations in units of mixing ratio (volume per volume) or molecules per cubic centimeter. Air densities in the model range from 2.53x10^19 to 2.62x10^19 molecules cm^-3 depending on altitude and time of day.

2.1. Dynamical Model

The vertical structure of the boundary layer is resolved with six layers extending from the valley floor to the inversion base, which is located at a constant altitude of 400 m AGL and which constitutes the upper boundary of the model domain (Figure 1). The dew point is fixed at 7°C, and layer 1 temperatures are assumed to range from 8°C (night) to 9°C (day), on the basis of observations from the Bakersfield National Weather Service station [National Climatic Data Center, 1984]. Temperatures in the upper layers are calculated from the adiabatic cooling rate; when saturation is reached, the excess water vapor condenses to form a non precipitating cloud (Figure 2). The cloud thicknesses and liquid water contents computed in this manner are consistent with the observations of JMWH.

Vertical transport within the cloud-topped boundary layer is simulated as an eddy diffusion process, which should be a reasonable approximation since updraft velocities in stratus clouds are relatively low. A constant and uniform eddy diffusion coefficient $K_v = 1x10^5 \text{ cm}^2 \text{s}^{-1}$ is assumed [Roach et al., 1982; Caughey et al., 1982]. The entrainment velocity at cloud top is fixed at $V_e = 0.2 \text{ cm s}^{-1}$ in order to provide a boundary layer residence time (2.3 days) consistent with the observed time constant for accumulation of CO at the Kernridge site on the west side of the valley.

Fig. 1. The San Joaquin Valley of California: model domain and one-dimensional vertical grid. The 300-m contour (altitude above sea level) delineates the edge of the valley. The model domain (thick line) consists of the four NAPAP 5.2 grid boxes (thin lines) encompassing Bakersfield and the surrounding area. The shaded area outlines the region of maximum SO2 emissions (0.3-0.6 tons km^-2 d^-1 [Aerovironment, Inc., 1984]). The vertical structure of the boundary layer is resolved with six layers extending from the ground to the inversion base (400 m above ground level). Layers 4-6 are cloudy at all times; layer 3 is cloudy at night but clear in the daytime.

Fig. 2. Simulated cloud liquid water content (grams per cubic meter) as a function of altitude and time of day. The thick line is the cloud boundary.
TABLE 2. Initial and Upper Boundary Conditions

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<tr>
<td>N(V)</td>
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<td>a</td>
</tr>
<tr>
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<tr>
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<td>Mn</td>
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<td>Cu</td>
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<td>Na⁺</td>
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<tr>
<td>SO₂</td>
<td>1</td>
<td>0.1</td>
<td>c</td>
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Notes: 
a. Initial concentrations are taken from measurements at Bakersfield on January 3 at 0000-0400 local time (JMWH).
b. Concentrations are held fixed throughout the simulation at their initial values, which are taken from the mean fog water concentrations observed in Bakersfield during the January 1984 experiment scaled by the liquid water content (JMWH). The values shown in the table are total atmospheric concentrations; in the case of trace metals, we assume that the soluble fraction represents 30% of this total. The initial partitioning of Fe, Mn, and Cu between oxidation states is 50/50 for Fe(II)/Fe(III), 10/90 for Cu(I)/Cu(II), and 60/40 for Mn(II)/Mn(III). This partitioning evolves over the course of the simulation as a result of aqueous-phase reactions. c. Initial concentrations are taken from measurements at Kernridge on January 3 at 0000 local standard time (JMWH). Upper boundary conditions are typical regional background concentrations.

(JMWH). Such an entrainment velocity is within the range observed in stratus clouds [Roach et al., 1982]. The air entrained into the boundary layer from the top is assumed to contain background pollutant concentrations, taken when available from measurements at mountain sites above the valley (Table 2). Deposition velocities are fixed at 1 cm s⁻¹ for all oxidants (e.g., O₃, NO₂, PAN) and water-soluble gases (e.g., HNO₃, NH₃, SO₂, RCOOH, RCHO, ROOH), and at 0.1 cm s⁻¹ for (SO₄²⁻, NO₃⁻, S(IV)²⁻, NH₂) aerosol [Walcek et al., 1987]. Other species (e.g., NO, alkanes, alkenes) are not removed by deposition.

The model domain is a 40 km x 40 km region defined by the four National Acid Precipitation Assessment Program (NAPAP) grid boxes encompassing Bakersfield and the immediately surrounding area (Figure 1). The domain is assumed to be well mixed horizontally and not ventilated by advection. The assumption of horizontal mixing has some justification since horizontal transport in the valley during stagnation episodes is contributed mostly by small-scale eddies and katabatic flows near the mountain slopes, which are diffusive rather than advective on a 40-km spatial scale [Reible, 1982]. The size of the model domain accounts for appropriate horizontal diffusion of pollutants emitted from the city of Bakersfield and from the oil fields immediately to the north; it excludes the town of Wasco where measured aerosol concentrations during the stagnation episode were significantly lower than at Bakersfield (JMWH).

Pollutant emissions are taken from the NAPAP 5.2 1980 hourly emission inventory for a winter weekday [Environmental Protection Agency, 1986], averaged over the four grid boxes of the model domain. The January 3-5, 1984 episode extended from a Tuesday to a Thursday, i.e., over weekdays only; therefore we assume that pollutant emissions did not vary from day to day. The 24-hour average emission rates for NOx, nonmethane hydrocarbons, and CO are 5.7x10¹¹ molecules cm⁻² s⁻¹, 1.6x10¹² molecules C cm⁻² s⁻¹, and 1.9x10¹² molecules cm⁻² s⁻¹, respectively. Modified emission rates are used for SO₂, NH₃, and organic acids. For SO₂ we assume a constant emission rate of 6.7x10¹¹ molecules cm⁻² s⁻¹, which is the 24-hour average value given in a detailed 1984 inventory of the model domain [Aeromonitor, Inc., 1984]. This value is about half the NAPAP value, reflecting a real decrease in SO₂ emissions between 1980 and 1984 due to the installation of scrubbers (F. Hagist, Texaco Oil Company, personal communication, 1984). High NH₃ emissions are expected from agricultural and livestock activities around Bakersfield, but no local emission inventory is available. We assume a constant NH₃ emission rate of 2.5x10¹² molecules cm⁻² s⁻¹, which was adjusted to fit the N(III) concentrations observed at Bakersfield. This emission rate is reasonably consistent with the mean value of 4.1x10¹¹ molecules cm⁻² s⁻¹ estimated by Jacob [1985] for the eastern San Joaquin Valley on the basis of livestock populations, fertilizer use, and soil types. Vehicular emissions of formic and acetic acids are included in the model on the basis of measured RCOOH/CO₂ emission ratios for automobile exhaust [Taijbo et al., 1988].

2.2. Aqueous-Phase Chemical Mechanism

Additions and modifications to the Jacob [1986] mechanism are listed in Table 3. The main changes are (1) addition of transition metal chemistry and (2) revision of sulfur chemistry to incorporate new kinetic data. Rate constants for ion reactions are corrected for ionic strength with the Debye-Hückel equation, and equilibrium constants are corrected with the Davis equation [Shum and Morgan, 1981]. The cloud water ionic strengths in the simulation are of the order of 0.01-0.1 M; therefore ionic strength corrections are necessary. The aqueous-phase redox reactions of NO, NO₂, and CO₂ have been deleted from the original Jacob [1986] mechanism because they play a negligible role in the model chemistry. The aqueous-phase chemistry of NO₃ is also ignored in view of evidence that the solubility of NO₃ in water is low [Mozurkevich, 1986].

Redox reactions of dissolved trace metals can play important roles in the oxidation of S(IV) and in the odd hydrogen budget [Graedel et al., 1986]. Our simulation of aqueous-phase transition metal chemistry draws heavily from the work of Graedel et al. [1986] and Wechsler et al. [1986] and includes a number of modifications and updates. We assume that Fe, Mn, and Cu are the only transition metals chemically active in the aqueous phase and that their reactivities are those of the redox couples Fe(II)/Fe(III), Mn(II)/Mn(III), and Cu(I)/Cu(II). From equilibrium considerations, we expect Fe(II), Mn(II), Cu(I), and Cu(II) in cloud water to be mainly present as free ions [Hoffmann and Jacob, 1984; Wechsler et al., 1986], while Fe(III) and Mn(III) should be in complexed form. Iron(III) forms hydroxy and sulfate complexes and precipitates as Fe(OH)₃ at high pH; we assume that all soluble Fe(III) complexes have similar reactivities and that
Fe(OH)$_3$ is chemically inert. The fraction of precipitated Fe(III) is computed from the equilibria in Table 3. Manganese(III) should mainly present as the hydroxy complex Mn(OH)$_3^+$, whose reactivity differs substantially from that of Mn$^{2+}$ [Davies, 1969]. When available, reaction rate constants specific to Mn(OH)$_3^+$ are used in the mechanism.

Oxidation of S(V) by Fe(III) and Mn(II) can be an important source of S(VI) at the concentration and pH ranges found in clouds [Jacob and Hoffmann, 1983]. By comparison, oxidation by Cu(II) is negligibly slow at pH < 7 [Conklin and Hoffmann, 1988b]. The mechanism of the S(IV) + Fe(III) reaction is still the subject of controversy. Conklin and Hoffmann [1988a] proposed a nonradical mechanism in which Fe(III) acts as a catalyst for the autoxidation of S(IV):

$$\text{H}_2\text{O}_2 \rightarrow \text{SO}_4^{2-} + \text{Fe}(\text{III}) \rightarrow \text{SO}_4^{2-} + \text{Fe}(\text{III}) + \text{H}_2\text{O}$$

This mechanism produces H$_2$O$_2$ which then reacts with S(IV), effectively doubling the S(VI) yield. However, Martin [1988] found evidence for radical formation in the S(IV) + Fe(III) reaction. He proposed a radical mechanism in which S(IV) is directly oxidized by Fe(III),

$$\text{SO}_2^{2-} + \text{Fe}(\text{III}) \rightarrow \text{SO}_4^{2-} + \text{Fe}(\text{II})$$

initiating the radical-assisted S(IV) oxidation chain propagated by reactions of SO$_2^{2-}$, SO$_3$, SO$_2$, and Cl$_2$.

The choice of mechanism for the S(IV) + Fe(III) reaction has two important implications for calculating S(VI) production rates. First, the yield of S(IV) is likely to depend on the mechanism. Second, the radical mechanism reduces Fe(III) while the nonradical mechanism does not. If the radical mechanism is correct, then Fe(II) must be reoxidized by a separate route in order to sustain the S(IV) + Fe(III) reaction. In the standard simulation we assume that both the S(IV) + Fe(III) and the S(IV) + Mn(II) reactions follow the nonradical mechanism. A sensitivity calculation will be conducted using the radical mechanism.

Gas-droplet transfer fluxes are computed for a monodisperse cloud with droplet radius of 10 µm, and mass accommodation coefficients $\gamma = 0.1$ for all soluble species. The assumption of $\gamma = 0.1$ yields accurate fluxes as long as the actual value of $\gamma$ ranges between 0.05 and 1 [Jacob, 1986]. Recent measurements indicate that mass accommodation coefficients of highly soluble species fall within this range, namely, $\gamma_{\text{SO}_2} = 0.11$ and $\gamma_{\text{HNO}_3} = 0.18$ on clean water droplets [Worsnop et al., 1989], $\gamma_{\text{SO}_2}$ > 0.2 on aqueous (NH$_4$)$_2$SO$_4$ aerosol [Mozurkewich et al., 1987], and $\gamma_{\text{OH}}$ = 1 on ice and H$_2$SO$_4$ surfaces [Gershenzon et al., 1986]. Accommodation coefficients for less soluble species such as O$_3$ may be much lower [Tang and Lee, 1987], but these species equilibrate rapidly between the gas and droplet phases so accurate computation of transfer fluxes is less important [Chameides, 1984; Schwartz, 1988].

2.3. Radiation Field

Calculation of photolysis rates requires solution to the equation of radiative transfer for an atmosphere containing a cloud layer. Most previous photochemical models have avoided this difficulty by assuming arbitrary correction factors which were applied to the clear-sky photolysis rate constants [Chameides and Davis, 1982; Graedel and Goldberg, 1983; Schwartz, 1984; Jacob, 1986; McElroy, 1986a; Graedel et al., 1986]. One exception is Chang et al. [1987], who computed the radiation field in the cloudy atmosphere using the delta-Eddington approximation [Joseph et al., 1976]. We present here a more comprehensive method of solving for the radiation field in an inhomogeneous, Mie-scattering, plane-parallel atmosphere (simulating a stratus cloud). The technique is based on the multi-stream method of Feautrier [1964] which has been extended to the general case of anisotropic scattering by L. H. Auer and M. J. Prather (unpublished, see applications by Coehran and Trafton, [1978] and Logan et al., [1981]). In this section we summarize the physical and optical properties of the cloud entering into the calculation of photolysis rates, and present results specific to the simulation of the Bakersfield episode. Complete descriptions of the optical properties of the cloud derived from Mie theory, and of the method of solving the equation of radiative transfer, are presented in the appendix. Also shown in the appendix are detailed calculations which highlight the critical variables controlling photolysis rates in the presence of planar clouds.

For the purpose of calculating the UV and visible radiation field, the cloud is treated as a polydisperse gamma distribution of spheres of pure H$_2$O with an effective radius of 10 µm. Such a distribution is typical of water clouds and gives a Mie scattering function that is only weakly dependent on wavelength [see Deirmendjian, 1969]. (N.B., computation of gas-droplet mass transfer rates in the chemical model assumes for convenience a monodisperse cloud with droplet radius of 10 µm; cf. section 2.2.) The total liquid water column of the daytime stratus cloud in the simulation is 24 g m$^{-2}$ (Figure 2), so that the vertically integrated geometric cross section per unit area for the assumed droplet size distribution is 1.8 (dimensionless: m$^2$ m$^{-2}$).

The optical properties of the cloud are derived from Mie-scattering theory for spheres of pure H$_2$O, assuming that all light is unpolarized (A. Lacis, Goddard Institute of Space Studies, personal communication, 1988; cf. Hansen and Travis, [1974]). The Mie phase function has a strong forward peak associated with diffraction of light around the droplets that cannot be adequately resolved by decomposition of the phase function into orthogonal polynomials, and is therefore truncated (i.e., very small angle scattering is treated as a non-event). For this renormalized phase function, the ratio of optical to geometric cross section, Q, is about unity for wavelengths between 300 and 600 nm (instead of 2 for the true Mie phase function), and the total optical depth of the cloud ($\tau_\text{opt}$) is about 2 instead of 4 (cf. appendix).

The solution for the radiation field in the cloudy atmosphere uses an 80-stream approximation to the Mie phase function. The atmospheric is assumed to consist of 900 mbar of clear, Rayleigh scattering atmosphere above the stratus cloud and 100 mbar below it; molecular scattering and absorption within the cloud are ignored. The total Rayleigh optical depth ranges from 1.0 at 310 nm to 0.3 at 400 nm, and the renormalized optical depth of the cloud, as noted above, is assumed to be 2.0. At 310 nm, stratospheric ozone has an absorption optical depth of about 1 that is included in the uppermost layers. A ground reflectivity (Lambertian) of 0.10 is assumed.

In the photochemical model the photolysis rates are calculated on-line with an algorithm which includes the effects of ozone absorption and molecular scattering [Prather, 1974; Logan et al., 1981], but not clouds. The computation is similar to that described in the appendix except that scattering is resolved by a six-stream Rayleigh phase function, rather than by the 80-stream Mie phase function. The simulation of cloud scattering is computationally more expensive by 2 orders of magnitude; we choose therefore to conduct these calculations off-line and use the results to define correction factors which are applied in the photochemical model to the clear-sky photolysis rates calculated for the Rayleigh atmosphere. The correction factors are the ratios of the monochromatic radiation intensities (J values) for the cloudy at-

<table>
<thead>
<tr>
<th>Compound</th>
<th>$K_{H298}$, M atm$^{-1}$</th>
<th>$\Delta H_{298}$, kcal mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$C(O)CHO</td>
<td>3.7(3)*</td>
<td>-15.0</td>
<td>Betterton and Hoffmann [1988a]</td>
</tr>
<tr>
<td>CH$_3$C(O)OOH</td>
<td>4.7(2)</td>
<td>-12.3</td>
<td>Lind and Kok [1986]</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>8.8(3)</td>
<td>-12.8</td>
<td>Weast [1986]</td>
</tr>
<tr>
<td>CHOCHO</td>
<td>3.5(5)*</td>
<td>0.*</td>
<td>Betterton and Hoffmann [1988a]</td>
</tr>
<tr>
<td>HNO$_4$</td>
<td>2.4(4)</td>
<td>0.*</td>
<td>Park and Lee [1987]</td>
</tr>
</tbody>
</table>

Read 3.7(3) as 3.7 x 10$^3$. Reaction rates are first-order in each of the species on the left-hand of the reaction equation, to the exclusion of other species. Species above the reaction sign are reactants which do not enter into the rate expression, generally because they are involved in a non limiting step of the overall reaction. Estimated values are flagged with an asterisk. Unknown activation energies are estimated as described by Jacob (1986).

$^a$ Equilibrium with the hydrated form: CH$_3$COCHO(g) = CH$_3$COCH(OH)$_2$.

$^b$ Lower limit for equilibrium with the hydrated forms GLYXA (cf. Table 1).

mosphere to the corresponding J values for clear sky and are determined locally as a function of the renormalized total cloud optical depth ($\tau_{tot}$), the overhead cloud optical depth for the particular layer ($\tau(z) < \tau_{tot}$) and the solar zenith angle ($\theta = \cos^{-1}x$). The value of $\tau(z)$ is computed by adding the renormalized optical depths $\Delta \tau$ of the individual cloudy layers overhead; $\Delta \tau$ is related to the liquid water content of the layer, W (grams of liquid water per cubic meter of air) and the layer thickness, $\Delta Z$ (meters), as follows (cf. appendix):

$$\Delta \tau = 0.08WAZ$$

The correction factor at 310 nm is applied to the rate of the photolysis reaction O$_3$ + hv $\rightarrow$ O$_2$ + O$^3$D, and the correction factor at 400 nm is applied to all other photolysis rates. Figure 3 shows the correction factors in the simulation at noon, as a function of altitude.

Aqueous-phase photolysis rates are determined by the radiation field within the cloud droplets, which can differ substantially from that outside because of reflection and refraction at the air-droplet interface and because of internal reflections within the droplet. Madronich [1987] computed a radiative enhancement of 57% within a pure water droplet relative to outside as a result of refraction and internal reflections. We did not include this radiative enhancement in the model calculations; the effect on model results is insignificant since aqueous-phase photolysis reactions play only a minor role in the chemistry of interest.

2A. Below-Cloud Aerosol

The below-cloud aerosol is simulated as a chemically inert mixture of aqueous ammonium salts ((NH$_4$)$_2$SO$_4$, NH$_4$S(IV), NH$_4$NO$_3$), trace metals (Fe, Mn, Cu), and NaCl. This aerosol is explicitly included in the model in order to (1) simulate the transport of non-volatile species below cloud base, (2) supply the nuclei for cloud droplet formation, and (3) account for the partitioning of N(III) and N(V) between the gas phase and the aerosol in

TABLE 3b. Modifications and Additions to the Jacob [1986] Aqueous-Phase Equilibria

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$K_{298}$, M$^a$</th>
<th>$\Delta H_{298}$, kcal mol$^{-1}$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$COCHO + H$_2$O = CH$_3$COCH(OH)$_2$</td>
<td>2.7(3)</td>
<td>0.*</td>
<td>Wasa and Musher [1970]</td>
</tr>
<tr>
<td>HNO$_4$ = NO$_3^+$ + H$^+$</td>
<td>1.0(2)</td>
<td>0.*</td>
<td>Park and Lee [1987]</td>
</tr>
<tr>
<td>Fe$^{2+}$ + OH$^-$ = Fe(OH)$_2$</td>
<td>3.2(4)</td>
<td>0.*</td>
<td>Turner et al. [1981]</td>
</tr>
<tr>
<td>Fe$^{3+}$ + SO$_4^{2-}$ = FeSO$_4^+$</td>
<td>1.4(4)</td>
<td>6.2</td>
<td>Sillen and Martell [1964]</td>
</tr>
<tr>
<td>Fe$^{3+}$ + SO$_4^{2-}$ = FeSO$_4^+$</td>
<td>4.0(6)</td>
<td>0.*</td>
<td>Conklin and Hoffmann [1988a]</td>
</tr>
<tr>
<td>Fe(OH)$_2$ + SO$_4^{2-}$ = FeHOSO$_3$</td>
<td>2.0(7)</td>
<td>0.*</td>
<td>Conklin and Hoffmann [1988a]</td>
</tr>
<tr>
<td>Fe$^{3+}$ + OH$^-$ = Fe(OH)$_2$</td>
<td>6.3(11)</td>
<td>-6.3</td>
<td>Flynn [1984]</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 2OH$^-$ = Fe(OH)$_3$</td>
<td>2.0(22)</td>
<td>-4.6</td>
<td>Flynn [1984]</td>
</tr>
<tr>
<td>Fe$^{3+}$ + 3OH$^-$ = Fe(OH)$_3$</td>
<td>1.3(37)</td>
<td>-20.7</td>
<td>Flynn [1984]; Latimer [1952]</td>
</tr>
<tr>
<td>Mn$^{2+}$ + OH$^-$ = Mn(OH)$_2$</td>
<td>2.5(14)</td>
<td>-8.5</td>
<td>Smith and Martell [1976]</td>
</tr>
</tbody>
</table>

Read 2.7(3) as 2.7 x 10$^3$. Reaction rates are first-order in each of the species on the left-hand of the equation reaction, to the exclusion of other species. Species above the reaction sign are reactants which do not enter into the rate expression, generally because they are involved in a non limiting step of the overall reaction. Estimated values are flagged with an asterisk. Unknown activation energies are estimated as described by Jacob (1986).
TABLE 3c. Modifications and Additions to the Jacob [1986] Aqueous-Phase Chemistry Mechanism: Aqueous-Phase Reaction Rate Constants

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_{298}$</th>
<th>$E_a$</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbons</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_3$COOH + OH $\rightarrow$ HO$_2$ + CO + CH$_3$O + H$_2$O</td>
<td>2.7(1)</td>
<td>3.7*</td>
<td>Pharataziz and Ross [1977]</td>
</tr>
<tr>
<td>CH$_3$COO$^-$ + OH $\rightarrow$ O$_2$ + CO + CH$_3$O + H$_2$O</td>
<td>8.7(1)</td>
<td>3.5*</td>
<td>Pharataziz and Ross [1977]</td>
</tr>
<tr>
<td>GLYXA + OH $\rightarrow$ HO$_2$ + 2CO + nH$_2$O</td>
<td>4.8(8)</td>
<td>3.5*</td>
<td>Pharataziz and Ross [1977]</td>
</tr>
<tr>
<td>MGLYA + OH $\rightarrow$ CH$_3$CO$_3$ + CO + nH$_2$O</td>
<td>4.8(8)*</td>
<td>3.5*</td>
<td>a</td>
</tr>
<tr>
<td>Odd Nitrogen</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$ $\rightarrow$ HNO$_2$ + O$_2$</td>
<td>1.2(2)</td>
<td>0*</td>
<td>Park and Lee [1987]</td>
</tr>
<tr>
<td>NO$_2$ $\rightarrow$ NO$_3$ + O$_2$</td>
<td>1.2(2)</td>
<td>0*</td>
<td>Park and Lee [1987]</td>
</tr>
<tr>
<td>Sulfur</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GLYXA + HSO$_3^-$ $\rightarrow$ GMBS</td>
<td>1.3(-1)</td>
<td>14.9*</td>
<td>Olson and Hoffmann [1988]</td>
</tr>
<tr>
<td>GLYXA + SO$_2^+$ $\rightarrow$ GMBS + OH$^-$</td>
<td>2.1(3)</td>
<td>9.2*</td>
<td>Olson and Hoffmann [1988]</td>
</tr>
<tr>
<td>GMBS + SO$_4^{2-}$ $\rightarrow$ GDBS</td>
<td>2.0(4)</td>
<td>7.8*</td>
<td>b</td>
</tr>
<tr>
<td>GDBS $\rightarrow$ GMBS + HSO$_3^-$</td>
<td>1.1(-5)</td>
<td>0*</td>
<td>Olson and Hoffmann [1988]</td>
</tr>
<tr>
<td>GDBS + OH$^-$ $\rightarrow$ GMBS + SO$_2^+$ + H$_2$O</td>
<td>8.8(6)</td>
<td>4.2*</td>
<td>Olson and Hoffmann [1988]</td>
</tr>
<tr>
<td>GMBS $\rightarrow$ GLYXA + HSO$_3^-$</td>
<td>4.6(-6)</td>
<td>0*</td>
<td>Olson and Hoffmann [1988]</td>
</tr>
<tr>
<td>GMBS + OH$^-$ $\rightarrow$ GLYXA + SO$_4^{2-}$ + H$_2$O</td>
<td>9.75(5)</td>
<td>5.5*</td>
<td>Olson and Hoffmann [1988]</td>
</tr>
<tr>
<td>MGLYA + HSO$_3^-$ $\rightarrow$ HAMS</td>
<td>1.3(0)</td>
<td>6.9</td>
<td>Betterton and Hoffmann [1987]</td>
</tr>
<tr>
<td>MGLYA + SO$_2^+$ + H$_2$O $\rightarrow$ HAMS + OH$^-$</td>
<td>1.4(5)</td>
<td>4.4</td>
<td>Betterton and Hoffmann [1987]</td>
</tr>
<tr>
<td>HAMS + OH$^-$ $\rightarrow$ MGLYA + SO$_2^+$ + H$_2$O</td>
<td>1.3(7)</td>
<td>-1.2</td>
<td>c</td>
</tr>
<tr>
<td>HAMS $\rightarrow$ MGLYA + HSO$_3^-$</td>
<td>4.2(-6)</td>
<td>19.6</td>
<td>Betterton and Hoffmann [1987]</td>
</tr>
<tr>
<td>SO$_2^+$ + O$_2$ + 2H$_2$O $\rightarrow$ SO$_3^+$ + H$_2$O$_2$ + 2OH$^-$</td>
<td>8.2(1)</td>
<td>11.*</td>
<td>Sadat-Shafai et al. [1981]</td>
</tr>
<tr>
<td>HSO$_3^-$ + OH$^-$ $\rightarrow$ SO$_3^+$ + H$_2$O</td>
<td>4.5(9)</td>
<td>3.4*</td>
<td>Huie and Neta [1987]</td>
</tr>
<tr>
<td>SO$_2^+$ + OH$^-$ $\rightarrow$ SO$_3^+$ + OH$^-$</td>
<td>5.2(9)</td>
<td>3.4*</td>
<td>Huie and Neta [1987]</td>
</tr>
<tr>
<td>HAMS + OH$^-$ $\rightarrow$ CH$_3$O + SO$_3^+$ + H$_2$O</td>
<td>1.3(9)</td>
<td>3.4*</td>
<td>Martin et al. [1989]</td>
</tr>
<tr>
<td>GMBS + OH$^-$ $\rightarrow$ SO$_3^+$ + GLYXA + H$_2$O</td>
<td>1.3(9)*</td>
<td>3.4*</td>
<td>d</td>
</tr>
<tr>
<td>GDBS + OH$^-$ $\rightarrow$ SO$_3^+$ + HSO$_3^-$ + GLYXA + H$_2$O</td>
<td>1.3(9)*</td>
<td>3.4*</td>
<td>d</td>
</tr>
<tr>
<td>HAMS + OH$^-$ $\rightarrow$ SO$_3^+$ + MGLYA + H$_2$O</td>
<td>1.3(9)*</td>
<td>3.4*</td>
<td>d</td>
</tr>
<tr>
<td>HSO$_3^-$ + Cl$_2$ $\rightarrow$ SO$_3^+$ + 2Cl$^-$ + H$^+$</td>
<td>3.4(8)</td>
<td>3.4*</td>
<td>Huie and Neta [1987]</td>
</tr>
<tr>
<td>SO$_2^+$ + Cl$_2$ $\rightarrow$ SO$_3^+$ + 2Cl$^-$</td>
<td>3.4(8)</td>
<td>3.4*</td>
<td>Huie and Neta [1987]</td>
</tr>
<tr>
<td>CH$_3$C(O)OH + HSO$_3^-$ + H$^+$ $\rightarrow$ CH$_3$COOH + SO$_2^+$ + 2H$_2$O</td>
<td>7.0(2)</td>
<td>7.9</td>
<td>Lind et al. [1987]</td>
</tr>
<tr>
<td>CH$_3$C(O)OH + HSO$_3^-$ $\rightarrow$ CH$_3$COOH + SO$_2^+$ + H$^+$</td>
<td>7.0(2)</td>
<td>7.9</td>
<td>Lind et al. [1987]</td>
</tr>
<tr>
<td>HSO$_3^-$ + HSO$_3^-$ + H$^+$ $\rightarrow$ 2SO$_2^+$ + 3H$^+$</td>
<td>7.1(6)</td>
<td>6.2</td>
<td>Betterton and Hoffmann [1988]*</td>
</tr>
<tr>
<td>SO$_2^+$ + HSO$_3^-$ $\rightarrow$ SO$_3^+$ + SO$_2^+$ + H$^+$</td>
<td>7.5(4)</td>
<td>7.9*</td>
<td>Huie and Neta [1987]</td>
</tr>
<tr>
<td>SO$_2^+$ + HSO$_3^-$ $\rightarrow$ SO$_2^+$ + SO$_2^+$ + H$^+$</td>
<td>7.5(4)</td>
<td>7.9*</td>
<td>Huie and Neta [1987]</td>
</tr>
<tr>
<td>SO$_2^+$ + SO$_2^+$ $\rightarrow$ 2SO$_2^+$ + O$_2$</td>
<td>6.0(8)</td>
<td>3.4*</td>
<td>Huie and Neta [1987]</td>
</tr>
<tr>
<td>Fe(III)$_{aq}$ + SO$_3^+$ + H$_2$O$_2$ $\rightarrow$ Fe(III) + SO$_2^+$ + H$_2$O$_2$</td>
<td>9.6(7)</td>
<td>12.*</td>
<td>f</td>
</tr>
<tr>
<td>Mn(II) + HSO$_3^-$ $\rightarrow$ Mn(II) + SO$_2^+$ + H$_2$O$_2$ + H$^+$</td>
<td>1.0(3)</td>
<td>17.8</td>
<td>g</td>
</tr>
<tr>
<td>SO$_2^+$ + Fe(III) $\rightarrow$ SO$_2^+$ + Fe(III)</td>
<td>9.9(8)</td>
<td>3.4*</td>
<td>Heckel et al. [1966]</td>
</tr>
<tr>
<td>SO$_2^+$ + Mn(II) $\rightarrow$ SO$_2^+$ + Mn(III)</td>
<td>1.8(10)</td>
<td>3.4*</td>
<td>Lee and Rochelle [1987]</td>
</tr>
<tr>
<td>SO$_2^+$ + Cu(I) $\rightarrow$ SO$_2^+$ + Cu(II)</td>
<td>9.9(8)</td>
<td>3.4*</td>
<td>h</td>
</tr>
<tr>
<td>SO$_2^+$ $\rightarrow$ SO$_2^+$ $\rightarrow$ SO$_2^+$ + H$^+$ + OH</td>
<td>3.6(2)</td>
<td>0*</td>
<td>Tang et al. [1989]</td>
</tr>
<tr>
<td>SO$_2^+$ + HSO$_3^-$ $\rightarrow$ SO$_2^+$ + H$^+$ + SO$_3^-$</td>
<td>7.5(8)</td>
<td>3.4*</td>
<td>Wine et al. [1989]</td>
</tr>
<tr>
<td>SO$_2^+$ + NO$_3^-$ $\rightarrow$ SO$_2^+$ + NO$_2$</td>
<td>9.8(8)</td>
<td>3.4*</td>
<td>Wine et al. [1988a]</td>
</tr>
<tr>
<td>SO$_2^+$ + CH$_3$OH $\rightarrow$ SO$_2^+$ + H$^+$ + CH$_3$O + HO$_2$</td>
<td>8.8(6)</td>
<td>4.2*</td>
<td>Wine et al. [1989]</td>
</tr>
<tr>
<td>SO$_2^+$ + HCOO$^-$ $\rightarrow$ SO$_2^+$ + CO$_2$ + HO$_2$</td>
<td>1.1(8)</td>
<td>3.4*</td>
<td>Wine et al. [1989]</td>
</tr>
<tr>
<td>SO$_2^+$ + HCOOH $\rightarrow$ SO$_2^+$ + CO$_2$ + HO$_2$ + H$^+$</td>
<td>4.6(5)</td>
<td>6.0*</td>
<td>Wine et al. [1989]</td>
</tr>
<tr>
<td>Reaction</td>
<td>$k_{298}$</td>
<td>$E_a$</td>
<td>Reference</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>-------</td>
<td>-----------</td>
</tr>
<tr>
<td>$\text{SO}_4^2- + \text{CH}_3\text{COO}^- \rightarrow \text{SO}_2^4- + \text{CO}_2 + \text{CH}_3\text{O}_2$</td>
<td>3.7(6)</td>
<td>4.7*</td>
<td>Wine et al. [1989]</td>
</tr>
<tr>
<td>$\text{SO}_4^2- + \text{CH}_3\text{COOH} \rightarrow \text{SO}_2^4- + \text{CO}_2 + \text{CH}_3\text{O}_2 + \text{H}^+$</td>
<td>1.4(4)</td>
<td>8.0*</td>
<td>Wine et al. [1989]</td>
</tr>
<tr>
<td>$\text{SO}_2^4- + \text{Cl}^- \rightarrow \text{SO}_2^4- + \text{Cl}^-$</td>
<td>2.6(8)</td>
<td>3.0</td>
<td>Wine et al. [1989]</td>
</tr>
<tr>
<td>$\text{Cl}^- \rightarrow \text{Cl}^- + \text{H}^+ + \text{OH}^-$</td>
<td>1.5</td>
<td>0.0</td>
<td>Wine et al. [1989]</td>
</tr>
</tbody>
</table>

Fe(II)/Fe(III)

Fe(II) + OH $\rightarrow$ Fe(III) + OH$^-$
$E_a$ = 3.8, 3.0 | Phataratiz and Ross [1977]

Fe(II) + HO$_2$ $\rightarrow$ Fe(III) + H$_2$O + OH$^-$
$E_a$ = 1.6(6), 5.4* | Rus and Bieksi [1985]

Fe(II) + O$_2$ 2H$_2$O $\rightarrow$ Fe(III) + H$_2$O + 2OH$^-$
$E_a$ = 1.0(7), 4.1* | Rus and Bieksi [1985]

Fe(OH)$^+$ + H$_2$O $\rightarrow$ Fe$^{3+}$ + OH + 2OH$^-$
$E_a$ = 1.5(6), 12.4 | Moffett and Zika [1987]

Fe(II) + O$_3$ $\rightarrow$ Fe(III) + OH + OH$^-$ + O$_2$
$E_a$ = 1.7(5), 6.5* | Conocchioli et al. [1965]

Fe(II) + Cl$_2$ $\rightarrow$ Fe(III) + 2Cl$^-$
$E_a$ = 1.0(7), 5.4 | Thornton and Laurence [1973] |

Fe(II) + HO$_2$ $\rightarrow$ Fe(III) + H$_2$O + 2OH$^-$
$E_a$ = 4.0(6), 7.5 | Thornton and Laurence [1973] |

Fe(III)$_{aq}$ + HO$_2$ $\rightarrow$ Fe(II) + H$^+$ + O$_2$
$E_a$ = 2.0(4), 7.8* | Bieksi et al. [1985]

Fe(III)$_{aq}$ + O$_2$ $\rightarrow$ Fe(II) + O$_2$
$E_a$ = 1.5(8), 3.0 | Rus and Bieksi [1985]

Fe$^{3+}$ + hv $\rightarrow$ Fe$^{2+}$ + OH + H$^+$
$E_a$ = 9.6(-7) | Weckler et al. [1986] |

Fe(OH)$^{2+}$ + hv $\rightarrow$ Fe$^{2+}$ + OH
$E_a$ = 5.9(-4) | Weckler et al. [1986] |

Fe(OH)$_2^+$ + hv $\rightarrow$ Fe$^{2+}$ + OH + OH$^-$
$E_a$ = 5.8(-4) | Weckler et al. [1986] |

Mn(II)/Mn(III)

Mn(II) + OH $\rightarrow$ Mn(III) + OH$^-$
$E_a$ = 3.4(7), 3.4* | Pick-Kaplan and Rabani [1976]

Mn(II) + HO$_2$ 2H$_2$O $\rightarrow$ Mn(III) + H$_2$O + OH$^-$
$E_a$ = 6.6, 4.4* | Cabelli and Bieksi [1984]

Mn(II) + O$_2$ 2H$_2$O $\rightarrow$ Mn(III) + H$_2$O + 2OH$^-$
$E_a$ = 1.1(8), 3.0* | Pick-Kaplan and Rabani [1976] |

Mn(II) + Cl$_2$ $\rightarrow$ Mn(III) + 2Cl$^-$
$E_a$ = 1.4(7), 8.1 | Lawrence and Thornton [1973] |

Mn(III) + HO$_2$ $\rightarrow$ Mn(II) + O$_2$ + H$^+$
$E_a$ = 2.0(4), 7.8* | k

Mn(III) + O$_2$ $\rightarrow$ Mn(II) + O$_2$
$E_a$ = 1.5(8), 3.0* | k

Mn(III) + H$_2$O $\rightarrow$ Mn(II) + HO$_2$ + H$^+$
$E_a$ = 3.2(4), 7.5* | Davies [1969] |

Mn(III) + Fe(II) $\rightarrow$ Mn(II) + Fe(III)
$E_a$ = 2.1(4), 7.8* | Davies [1969] |

Mn(III) + Cu(I) $\rightarrow$ Mn(II) + Cu(II)
$E_a$ = 2.1(4), 7.8* | l

Cu(II)/Cu(I)

Cu(I) + OH $\rightarrow$ Cu(II) + OH$^-$
$E_a$ = 3.8(9), 3.0* | m

Cu(I) + HO$_2$ 2H$_2$O $\rightarrow$ Cu(II) + H$_2$O + OH$^-$
$E_a$ = 1.5(9), 3.0* | Bieksi et al. [1985] |

Cu(I) + O$_2$ 2H$_2$O $\rightarrow$ Cu(II) + H$_2$O + 2OH$^-$
$E_a$ = 1.1(0), 3.0* | Rabani et al. [1973] |

Cu(I) + H$_2$O $\rightarrow$ Cu(II) + OH + OH$^-$
$E_a$ = 4.5, 6.2 | Moffett and Zika [1987] |

Cu(I) + Cl$_2$ $\rightarrow$ Cu(II) + 2Cl$^-$
$E_a$ = 1.4(7), 6.4* | n

Cu(II) + HO$_2$ $\rightarrow$ Cu(I) + O$_2$ + H$^+$
$E_a$ = 1.8, 3.0* | Rabani et al. [1973] |

Cu(II) + O$_2$ $\rightarrow$ Cu$^{2+}$ + O$_2$
$E_a$ = 5.9, 3.0* | Bieksi et al. [1985] |

Read 2.7(7) as 2.0x10$^7$. Reaction rates are first-order in each of the species on the left-hand of the reaction equation, to the exclusion of other species. Species above the reaction sign are reactants which do not enter into the rate expression, generally because they are involved in a non limiting step of the overall reaction. Estimated values are flagged with an asterisk. Unknown activation energies are estimated as described by Jacob [1986].

* The value for GLYX-A+OH is assumed.

* Derived from Olsen and Hoffmann [1988a] data for GMBS + HSO$_3^-$ = GBDS (K = 1.45x10$^4$ M) and GDBS + OH$^-$ → GMBS + HSO$_3^-$ (k = 8.8x10$^6$ M$^{-1}$ s$^{-1}$). We assume that the equilibrium GMBS + HSO$_3^-$ = GBDS represents a balance between forward reaction GMBS + SO$_2^4-$ and back reaction GDBS + OH$^-$ The rate constant for GMBS + SO$_2^4-$ is then given by kKw/Ka, where Kw and Ka are the acid dissociation constants for H$_2$O and HSO$_3^-$, respectively.

* Derived from Batterton and Hoffmann [1987] data for CH$_3$COOH(O$^-$)SO$_3^- \rightarrow$ CH$_3$COCHO + SO$_2^4-$ (k$_{q1}$ = 6.8x10$^4$ s$^{-1}$, E$_a$ = 16.9 kcal mole$^{-1}$) and CH$_3$COOH(OH)SO$_3^- \rightarrow$ CH$_3$COCHO(O$^-$)SO$_3^-$ + H$^+$ (K$_a$ = 1.9x10$^{-11}$ M, ΔH = -4.8 kcal mole$^{-1}$), and the H$_2$O acid dissociation constant. The negative value for the apparent E$_a$ results from the enthalpies of the participating equilibria.
The two oxidation states of each metal are transported as separate species, and the partitioning between the two states is allowed to evolve over the course of the simulation as a result of aqueous-phase reactions in the cloud.

Concentrations of Cl− are held fixed at the mean values observed in Bakersfield aerosol during the January 1984 field experiment (Table 2). A matching concentration of a chemically inert cation, e.g., Na+, is assumed. The species Cl−, Cl, and Cl2 are not transported separately in the model because (1) they are in rapid equilibrium with each other and (2) the contributions of Cl and Cl2 to total chlorine are small.

2.5. Computational Procedure

The results presented below are from 72-hour simulations beginning on January 3, 1984 at 0000 local time, which is defined as the onset of the stagnation episode. Initial concentrations (Table 2) are specified on the basis of observations when available, and from typical regional background concentrations otherwise. The model computes the chemical evolution of atmospheric composition in layer k by solving the general diffusion equations discretized in space for m independent gas-phase and aqueous-phase species. The value of m depends on whether layer k is cloudy or clear since aqueous-phase species are present only in cloud. The set of independent species includes all gas-phase species of the detailed Lurmann et al. [1986] mechanism, plus the class I and class II aqueous-phase species of Table 4. Aqueous-phase species in classes III-IV-V of Table 4 are treated as dependent variables, with concentrations constrained by equilibrium with the gas phase (class III), steady state (class IV), or the electroneutrality equation (class V). Use of computational constraints for aqueous-phase species in classes III-IV-V saves computer time at negligible loss in accuracy.

The change with time in the concentration n_{jk}(t) (molecules per cubic centimeter) of independent species i in layer k is given by

\[
\frac{dn_{jk}(t)}{dt} = P_{jk}[n_{jk}(t)] - L_{jk}[n_{jk}(t)]
- \frac{2K_1 <N_k>}{z_{j+1}-z_{j}} \left( \frac{n_{jk}(t)/N_k - n_{j+1,k}(t)/N_{j+1}}{z_{j+1}-z_{j}} \right)
- \frac{2K_{k-1} <N_{k-1}>}{z_{j}-z_{j-1}} \left( \frac{n_{jk}(t)/N_k - n_{j-1,k-1}(t)/N_{j-1}}{z_{j}-z_{j-1}} \right)
\] (2a)

The value for HMS+OH is assumed [Martin et al., 1989].
McElroy [1987] reports as preliminary values for this reaction \( k_{298} = 2.7 \times 10^7 \) M\(^{-2}\)s\(^{-1}\) and \( E_a = 1.2 \) kcal mol\(^{-1}\).
Stoichiometry from Conklin and Hoffmann [1988a], rate constant at zero ionic strength from Martin and Hill [1987a].
Rate constant at zero ionic strength from Martin and Hill [1987b], activation energy from Hoffmann and Calvert [1985].
Value for SO4 + Fe(II) is assumed.
Reaction proceeds by competing outer-sphere and inner-sphere pathways, with different activation energies.
Photolysis rates for 375m AGL (top of cloud) at noon. These values are the highest attained in the simulation.
Values for Fe(II) + O2(i-1) are assumed.
Value for Mn(OH)\(^{2+}\) + Fe\(^{2+}\) is assumed.
Value for Fe\(^{2+}\) + OH is assumed.
Value for Fe\(^{2+}\) + Cl\(^{-}\) is assumed.
TABLE 4. Partitioning of Aqueous-Phase Species Into Computational Classes

<table>
<thead>
<tr>
<th>Class</th>
<th>Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class I: independent species</td>
<td>( \text{O}_2^-(t), \text{OH}, \text{H}_2\text{O}_2^-, (\text{HCOOH} + \text{HCOO}^-), (\text{SO}_4^{(aq)} + \text{H}_2\text{SO}_4^+) ) GLYXA, ( \text{CH}_3\text{OOH} )</td>
</tr>
<tr>
<td>Evaporating to the gas phase</td>
<td></td>
</tr>
<tr>
<td>Class II: independent species</td>
<td>( \text{S(VI)}, \text{N(V)}, \text{N}(-\text{III}), \text{Fe(II)}, \text{Fe(III)}, \text{Mn(II)}, \text{Mn(III)}, \text{Cu(I)}, \text{Cu(II)}, \text{HMS}, \text{HAMS}, \text{GMBS}, \text{GDBS}, \text{HSO}_3, \text{Cl}^-, \text{Na}^+ )</td>
</tr>
<tr>
<td>evaporating to aerosol</td>
<td></td>
</tr>
<tr>
<td>Class III: species at equilibrium</td>
<td>( \text{CH}_3\text{O} + \text{H}_2\text{C}(-\text{OH})_2, \text{MGLYA}, (\text{HNO}_2 + \text{NO}_2) )</td>
</tr>
<tr>
<td>with gas phase</td>
<td>( \text{H}_2\text{CO}_3 + \text{HCO}_3^-, \text{CH}_3\text{OH}, (\text{CH}_3\text{COOH} + \text{CH}_3\text{COO}^-), \text{CH}_3\text{C}(-\text{O})\text{COOH} )</td>
</tr>
<tr>
<td>Class IV: species at steady state</td>
<td>( \text{SO}_3, \text{SO}_4^2-, \text{O}_3, (\text{Cl} + \text{Cl}_2), (\text{HNO}_4 + \text{NO}_3) )</td>
</tr>
<tr>
<td>Class V: species constrained by electroneutrality equation</td>
<td>( \text{H}^+, \text{OH}^- )</td>
</tr>
</tbody>
</table>

\[
\frac{dn_{i,j,k}(t)}{dt} = P_{i,j,k}[n_{i,j,k}(t)] - L_{i,j,k}[n_{i,j,k}(t)]
\]

where \( P_{i,j,k} \) and \( L_{i,j,k} \) are the chemical production and loss terms, respectively, which depend on the concentrations of the independent species \( j=1, m \) in layer \( k \); \( z_i \) is the layer midpoint; \( N_j \) is the air concentration (molecules per cubic centimeter) at altitude \( z_i \); \( <N_j> \) is the air concentration of the boundary layer between layers \( k \) and \( k+1 \); \( K_j <N_5> \) is the eddy diffusion coefficient between layer \( k \) and layer \( k+1 \); \( z_f \) is the upper boundary of the model domain; \( V_{e,j} \) is the deposition velocity; \( V_s \) is the entrainment velocity at \( z_f \); and \( n_{i,T} \) is the concentration at \( z_f \). The concentrations \( n_{i,k+1}(t) \) and \( n_{i,k-1}(t) \) in the eddy flux terms are identical to the actual concentrations \( n_{i,k-1}(t) \) and \( n_{i,k+1}(t) \) except in two cases: (1) Layer \( k \) is cloudy, layer \( k-1 \) is noncloudy, and \( i \) is a class I aqueous-phase species:

\[
n_{i,k-1}(t) = 0 \quad (3a)
\]

(2) Layer \( k \) is noncloudy, layer \( k+1 \) is cloudy, and \( i \) is a gas-phase species produced by evaporation of class I aqueous-phase species \( i' \):

\[
n_{i,k+1}(t) = n_{i,k-1}(t) + n_{i,k+1}(t) \quad (3b)
\]

The system of coupled equations (2) for all species and layers is integrated using an implicit finite difference method [Richmeyer, 1957], with time steps of 15 min in the daytime and 1 hour at night. Radiation intensities are recalculated at 30-min intervals. We established in test simulations that these time steps are sufficiently small to ensure stable and accurate solutions.

3. OVERVIEW OF RESULTS

3.1. Sulfate, Nitrate, Ozone, Organic Acids

We compare in Figure 4 the simulated and observed time evolutions of sulfate, nitrate, and ammonium aerosol concentrations. Model results agree well with observations, although in the case of \( \text{NH}_4^+ \) this agreement is forced by the adjustment of the \( \text{NH}_3 \) source. The sulfate aerosol measurements of JMWH could have suffered from positive bias due to oxidation of \( \text{SIV} \) aerosol on the filter or during the filter extraction procedure. To account for this possibility we show in Figure 4 the simulated concentrations of both \( \text{S(VI)} \) and \( \text{S(VI)} + \text{S(IV)} \). The \( \text{S(IV)} \) concentrations in the model are small compared to \( \text{S(VI)} \) concentrations; hence there is little difference between the two plots.

Sulfate accumulates progressively over the course of the episode, due to the combination of restricted ventilation and sustained production by \( \text{SO}_2 \) oxidation. The concentration of \( \text{SO}_4^2- \) increases rapidly at the beginning of the episode and reaches after 1 day a steady state level of 18 ppb (Figure 5) which reflects mainly a balance between emissions and deposition. Model results for \( \text{SO}_4^2- \) are reasonably consistent with the daily average \( \text{SO}_4^2- \) concentrations of 10-28 ppb measured on January 4-5 at Texaco monitoring stations in Oldale just north of Bakersfield [F. Hagist, Texaco Oil Company, personal communication, 1984]. The mean boundary layer \( \text{SO}_2 \) oxidation rate in the model is about 1% \( \text{h}^{-1} \) at noon and 2% \( \text{h}^{-1} \) at midnight; by comparison, JMWH estimated a range of 0.4-1.1% \( \text{h}^{-1} \) on the basis of observed \( \text{S(VI)} \) accumulation rates. Most of the \( \text{S(VI)} \) production in the model takes place in the
stratus cloud (Figure 6). The mechanisms for S(VI) production will be discussed in detail in section 4.

By contrast to sulfate, nitrate does not accumulate over the course of the stagnation episode, even though NOx concentrations rise to high levels both in the model (Figure 5) and in observations at Kernridge (JMWK). It appears that stagnant conditions do not provide a particularly favorable environment for the oxidation of NOx to N(V), for two reasons. First, odd hydrogen is depleted at high NOx concentrations, so that the rate of N(V) production by the reaction NOx + OH increases only slowly with increasing NOx concentration. Second, O3 is titrated at night by large excesses of freshly emitted NO, preventing formation of NO2 which is normally an important N(V) precursor in polluted atmospheres [Russell et al., 1986]. The only significant source of N(V) in the model is the reaction NO2 + OH; this reaction is fastest in the stratus cloud because the radiation intensities, and hence the OH concentrations, are maximum (Figure 6).

The depletion of O3 is a remarkable feature of the stagnation episode. Concentrations of O3 in the simulation peak at only 4-5 ppb in the daytime and fall to essentially zero at night (Figure 5); observations at Kernridge on January 3-5 show a similar pattern, with daytime maxima of 3-10 ppb and nighttime concentrations below the detection limit of 2 ppb (JMWK). The photochemical production of O3 within the boundary layer is inhibited by the accumulation of NOx to high levels, while downward transport of O3 from the free troposphere is restricted by the inversion. The low daytime O3 concentrations reflect this suppression of the O3 source combined with rapid removal of O3 by deposition. In a test simulation with NOx emissions reduced by half we found that the predicted daytime maxima of O3 nearly tripled, demonstrating the strong quenching effect of excessive NOx on O3 production. At night, O3 is depleted by reaction with NOx, and the subsequent deposition of NOx removes odd oxygen from the boundary layer.

The simulated concentrations of HCOOH and CH3COOH on model day 3 are 0.07 ppb and 0.04 ppb, respectively. By comparison, Munger et al. [1989] reported mean concentrations of 0.3 ppb for both acids at Bakersfield on the basis of simultaneous measurements of fog water concentrations, liquid water contents, and pH. Evidently, the model sources of organic acids are insufficient to account for these observations. In the model the major source of HCOOH is the aqueous-phase reaction H2C(OH)2 + OH, and the only significant source of CH3COOH is emission from automobile exhaust. Ozonation of olefins is not a significant source of either acid because (1) O3 concentrations are low, and (2) NO levels are sufficiently high that Criegee intermediates in the model react with NO instead of with H2O [Atkinson and Lloyd, 1984]. The missing source(s) of organic acids could be of agricultural origin, e.g., emissions from cattle waste [Jain et al., 1986] or atmospheric oxidation of insecticide fumigants [Tuazon et al., 1984]. Bacterial oxidation of aldehydes in cloud droplets is another possible source. The inability of the model to simulate organic acid concentrations should not compromise other model results because organic acids are negligible contributors to the total acid budget even at the concentrations reported by Munger et al. [1989].
3.2. Acid-Base Balance and Alkalinity

The rapid production of S(VI) in the model adds large amounts of acidity to the boundary layer atmosphere, but we find that this acidity is almost entirely neutralized by NH₃. Observations in Bakersfield indicate that NO₃⁻ and SO₄²⁻ in aerosol and fog water are generally 90-100% neutralized [Munger et al., 1983; Jacob et al., 1984; JMWH], in accord with model predictions. A striking feature of the Bakersfield observations, which is well simulated by the model, is that the total (aerosol + gas-phase) concentrations of acids and bases are usually in close balance. The equivalent ratio \( \frac{(S(VI))}{(N(V))} \), which provides an approximate measure of this balance, remains near unity throughout the stagnation episode both in the model and in the observations (Figure 7). It appears therefore that N(-III) is present in amounts just sufficient to neutralize the acidity; there is little NH₃(g) or HNO₃(g) present in excess of the neutral aerosol. We will propose in section 5 an explanation for this close balance between acids and bases.

A quantitative measure of the acid-neutralizing capacity of the atmosphere is the atmospheric alkalinity, (ALK), which represents the deficiency of H⁺ with respect to a reference "neutral" atmosphere. The concept of atmospheric alkalinity [Liljestrand, 1983; JMWH] is analogous to the concept of alkalinity commonly used in water chemistry [Stumm and Morgan, 1981]. We define here (ALK) by reference to the set of species (NH₃, NO₃⁻, SO₄²⁻, S(VI), CO₂, RCOOH, H₂O). The value of (ALK) is computed by summing the concentrations of proton acceptors with respect to the reference species, and subtracting the concentrations of proton donors:

\[
(ALK) = (NH_3(g)) + (HCOO^-) + (CH_3COO^-) + (HCO_3^-) - (HNO_3(g)) - (HSO_4^-) - (H_2SO_4^-) - (H^+) \tag{4}
\]

where all concentrations are in equivalent units. The contributions to (ALK) from HCOO⁻, CH₃COO⁻, and HCO₃⁻ are small compared to the contribution from NH₃(g); therefore (ALK) can be expressed to a good approximation by

\[
(ALK) = (N(-III)) - (N(V)) - (S(IV)) - (S(VI)) \tag{5}
\]

We show in Figure 8 the simulated vertical distributions of (ALK) at noon and midnight on model day 3, computed from equation (4). A remarkable result is that (ALK) changes sign within the boundary layer. The atmosphere near the ground contains net alkalinity, but the alkalinity decreases with altitude, and net inorganic acidity (negative alkalinity) is predicted for the upper portion of the boundary layer. The vertical trend of (ALK) reflects the opposite spatial distributions of NH₃ and acid sources: NH₃ is emitted at ground level, but S(VI) and N(V) are mostly produced within the cloud. From this result we draw the general conclusion that ground-based measurements of atmospheric acidity suffer from systematic bias because of the proximity of NH₃ sources. The air aloft may be acidic even though no net acidity is measured at the ground.

The small nonneutralized fraction of acidity in the simulated cloud is responsible for relatively low cloud water pH values, ranging from 4.2 at night to 3.4 in the early afternoon (Figure 9). The lower pH values in daytime are due mostly to gas-phase HNO₃ production by the reaction NO₂ + OH. The pH values predicted by the model can be compared to observations at McKittrick (Figure 1), where the cloud was sampled on January 3-5, 1984, as it intercepted the western slope of the valley. The measured cloud water pH values at McKittrick ranged from 2.7 to 5.2,
are due to depletion of the precursors HO₂ and O₂(-I), and to the rapid reaction of H₂O₂ with S(IV) in the aqueous phase. The diurnal variation of H₂O₂ concentrations is largely controlled by the rate of the S(IV) + Fe(III) reaction, which provides the main H₂O₂ source. At noon, production of H₂O₂ from O₂(-I) reduction by metal ions is comparable to production from the S(IV) + Fe(III) reaction (Figure 11), but the latter source is much faster at night when the cloud water pH is higher (section 4).

### 3.4. Sulfur(IV)

The simulated S(IV) cloud water concentrations on model day 3 range from 72 μM to 547 μM; the mean liquid water-weighted concentration is 131 μM. By comparison, the cloud water concentrations observed at McKittrick on January 3-5, 1984, ranged from 14 to 95 μM [Jacob, 1985], lower than predicted. Higher concentrations were observed in Bakersfield fogs sampled at other times during the January 1984 experiment (mean [S(IV)] = 384 μM; JMWH). Cloud water concentrations of S(IV) are strongly dependent on liquid water content and pH [Olson and Hoffmann, 1989]; therefore, simulation of observations is difficult. The fact that the simulated and observed values are within 1 order of magnitude suggests that the simulation may be reasonable.

We show in Figure 12 the time evolution of S(IV) concentrations in layer 6 (375 m AGL). Over 90% of total S(IV) is present as S(IV)-carbonyl complexes, with HMS by far the most abundant. This result is in harmony with the observation by Munger et al. [1986] that HMS is the main S(IV) species present in Bakersfield fog samples. Formation of HMS in the model is facilitated by the abundance of the precursor CH₂O, which accumulates quickly to a steady concentration of 7 ppb and is not depleted at night because of continuous supply from direct emissions. The CH₂O concentrations predicted by the model are consistent with the mean Bakersfield value of 10 ppb reported by Munger et al. [1989] on the basis of simultaneous measurements of fog water CH₂O concentrations and liquid water contents.

The HMS concentrations in the model increase rapidly at night and decrease slowly during the day (Figure 12). This pattern reflects mainly the enhanced production of HMS at night. The main source of HMS is the reaction of CH₂O with SO₃²⁻:

\[
\text{CH}_2\text{O} + \text{SO}_3^{2-} \rightarrow \text{OCH}_2\text{SO}_3
\]

followed by

\[
\text{OCH}_2\text{SO}_3 + \text{H}^+ \rightarrow \text{HOCH}_2\text{SO}_3
\]

### 3.3. Odd Hydrogen Chemistry

We show in Figure 10 the vertical distributions of gas-phase OH, HO₂, and HNO₃ concentrations at noon on model day 3. The OH concentrations are comparable to the clean air value computed by Logan et al. [1981] for that latitude and season, but the HO₂ concentrations are 2 orders of magnitude lower because of the high NO levels. The most abundant odd hydrogen species is HNO₃, whose formation is favored by the combination of high NO₃ levels and low temperatures. In cloud, HNO₃ is scavenged and decomposes to HNO₂ and O₂ in the aqueous phase [Park and Lee, 1987]. This aqueous-phase sink is faster than gas-phase thermal decomposition so that HNO₃ concentrations are a factor of 3 lower in the cloud than below. By contrast, OH and HO₂ concentrations are higher in the cloud because of the stronger radiation intensities (which enhance odd hydrogen production).

Figure 11 summarizes the cycling of odd hydrogen species in the cloud. We find that scavenging by cloud droplets contributes only a minor sink to the budgets of gas-phase OH and HO₂. This result is in stark contrast with model calculations of clouds in low-NO₂ atmospheres, where scavenging by cloud droplets is the main sink of HO₂ [Chameides and Davis, 1982; Schwartz, 1984; Jacob, 1986]. Under the high-NO₂ conditions simulated here, the gas-phase reaction of HO₂ with NO is fast compared to scavenging.

Cloud water concentrations of OH and O₂(-I) in Figure 11 are 1 to 2 orders of magnitude lower than values predicted for tropical clouds [Chameides and Davis, 1982; Jacob, 1986]. The depletion of O₂(-I) follows in part from the depletion of gas-phase HO₂ and in part from the rapid aqueous-phase reactions of O₂(-I) with metal ions. The depletion of OH is due mainly to the abundance of H₂C(OH)₂ (hydrated formaldehyde), since O₂(-I) produced from the reaction H₂C(OH)₂ + OH reacts with metal ions and is not recycled back to OH (Figure 11). In contrast, the reaction S(IV) + OH is not an efficient sink for OH because OH is recovered by the reaction Cl + H₂O in the subsequent oxidation chain (see section 4).

Concentrations of H₂O₂ in the boundary layer range from 2 to 5 ppt at noon and from 10 to 20 ppt at midnight; these low values
model concentrations of methylglyoxal (0.1-0.3 ppb) and glyoxal (0.1-0.4 ppb) compared to CH$_3$O. Another contributing factor is that the thermal dissociation reactions of HAMS, GMBS, and GDBS are relatively rapid. For example, HAMS has a lifetime of 1 hour against thermal dissociation at pH 4 and 6°C, compared to 150 days for HMS (cf. data in Table 3). The rapid nighttime decay of HAMS in the simulation (Figure 12) is caused by thermal dissociation following the removal of methylglyoxal by deposition.

4. SO$_2$ OXIDATION MECHANISMS

The contributions to S(VI) production from individual SO$_2$ oxidants are shown in Figure 13 for model day 3. Four mechanisms make significant contributions: (1) aqueous-phase autoxidation catalyzed by Fe(III), (2) aqueous-phase oxidation by H$_2$O$_2$, (3) gas-phase oxidation by OH, and (4) aqueous-phase oxidation by OH (including the ensuing S(IV) oxidation chain). Other aqueous-phase SO$_2$ oxidants such as Mn(II), O$_3$, CH$_3$OOH, CH$_3$C(O)COOH, and O$_3$- are negligible. The contribution from H$_2$O$_2$ follows closely that from Fe(III) because the main source of H$_2$O$_2$ is the S(IV) + Fe(III) reaction. In this section we examine the various factors controlling S(VI) production by the aqueous-phase reactions S(IV) + Fe(III) and S(IV) + OH.

4.1. S(IV) + Fe(III)

Sulfate production by the S(IV) + Fe(III) reaction is much faster at night than in the daytime (Figure 13), due mainly to the diurnal variation of pH and hence of the cloud water concentration of SO$_3$$^-$, the reactive S(IV) species. The cloud water concentrations of Fe(III) are higher in the daytime than at night because of the lower liquid water content, but this effect is canceled when sulfate

![Diagram](image)

Fig. 11. The odd hydrogen cycle in cloud (layer 6, model day 3 at noon). The main reaction pathways are indicated. Concentrations are in units of molecules per cubic centimeter of air, and transformation rates are in units of molecules per cubic centimeter of air per second. Aqueous-phase concentrations (M) are given in brackets. Organic peroxy radicals are not shown explicitly; under the high-NO$_2$ conditions simulated here, they react mainly with NO to eventually yield HO$_2$. 

![Graph](image)

Fig. 10. Vertical profiles of gas-phase OH, H$_2$O, and HNO$_4$ concentrations on model day 3 at noon.
production per unit volume of air is considered as in Figure 13. The Fe(II)/Fe(III) ratio shows little diurnal variation (Figure 14a).

The partitioning of iron between its two oxidation states in the model is largely controlled by the respective reactivities of Fe(II) and Fe(III) with O$_2$ from (Figure 14a). Oxidation of Fe(II) by O$_2$ is negligibly slow in the range of pH values found in cloud water [Sung and Morgan, 1980]. We find that most of the soluble iron is present as Fe(II); only a small fraction (10-15%) is present as Fe(III). This result is in contradiction with the raindrop chemistry model calculations of Graedel et al. [1986] in which Fe(III) was found to contribute 90% of total dissolved iron. The main reason for the contradiction is that Graedel et al. [1986] used for the Fe(II) + O$_2$ reaction a rate constant of 8.7 x 10$^5$ M$^{-1}$ s$^{-1}$ which was indirectly inferred by Matthews [1983] to explain an observed nonlinearity in the Fe(III) yield from the irradiation of FeSO$_4$ solutions at various concentrations. Since then the rate constant for the Fe(II) + O$_2$ reaction has been directly measured [Rush and Bielski, 1985] and found to be 80 times higher than the value given by Matthews [1983]. If Fe(II) is indeed the most abundant oxidation state of soluble iron in cloud water, as we argue here, then the cloud chemistry models based on the assumption that soluble iron is Fe(III) [Jacob and Hoffmann, 1983; Seigneur and Saxena, 1984] would seriously overestimate S(VI) production rates.

We conducted a sensitivity calculation in which the radical mechanism for the S(IV) + Fe(III) reaction was assumed, i.e., stoichiometry (R1) was replaced by stoichiometry (R2) in the chemistry code. The simulated S(IV) and S(VI) concentrations are shown in Figure 15. The concentrations of S(VI) are much lower than with the nonradical mechanism; by contrast, S(IV) accumulates to high levels. The S(IV) + Fe(III) reaction by the radical mechanism is the main sink for Fe(III), and is therefore self-inhibiting because of Fe(III) depletion (Figure 14b). The rate of

the S(IV) + Fe(III) reaction is limited by the rate of Fe(II) oxidation, which is slow due to the scarcity of radical oxidants. At night the production of S(VI) is insignificant, so that cloud water pH is maintained at a relatively high level (~ 5.0) which allows efficient production of HMS. After 3 model days, HMS contributes 70% of total aerosol sulfur (in equivalent units).

Although the nonradical and radical mechanisms predict very different S(VI) concentrations, one cannot discriminate between the two on the basis of S(VI) aerosol concentration measurements, because S(IV) was not preserved in the aerosol samples and therefore could have been oxidized to S(VI) during the interval between sample collection and analysis. A more reliable diagnostic is the measured S(VI)/S(VI) equivalent ratio in cloud water, since S(IV) was preserved in cloud water samples immediately upon collection (IMWH). The measured S(VI)/S(VI) ratios in the stratus clouds sampled at McKittrick were always less than 0.2, and in Bakersfield fog water they were less than 0.5 in 80% of the samples [Jacob, 1985]. These observations lend support to the non-radical mechanism.

4.2. S(IV) + OH

Aqueous-phase oxidation of S(IV) by OH initiates a chain reaction propagated by reactions of S(IV) with the radicals SO$_3^-$, SO$_4^-$, and Cl$_2^-$ [McElroy, 1986b]. A major uncertainty in assessing the chain length under atmospheric conditions is that the reactivity of HMS with the radical intermediates is unknown. We have assumed here that the S(IV)-carbonyl adducts do not react with SO$_3^-$, SO$_4^-$, or Cl$_2^-$, so that only HSO$_3^-$ is involved in chain propagation. The main steps of the reaction sequence, and their rates, are listed in Table 5. The chain is initiated by

(R5) \[ \text{S(IV)} + \text{OH} \rightarrow \text{SO}_3^- + \text{H}_2\text{O} + \text{products} \]

where it is assumed that oxidation of S(IV)-carbonyl adducts produces the SO$_3^-$ radical. Reaction (R5) is followed by rapid addition of O$_2$ to SO$_3^-$ [Huie and Neta, 1984]:

(R6) \[ \text{SO}_3^- + \text{O}_2 \rightarrow \text{SO}_5^- \]

The main sinks of SO$_3^-$ in atmospheric clouds are expected to be the reactions with O$_2$, HCOO$, and SO$_3^-$. [Jacob, 1986; Huie and Neta, 1987]. Reaction with HSO$_3^-$ is slow [Huie and Neta, 1987].
Fig. 14. Cycling of soluble iron between Fe(II) and Fe(III) in the simulation, assuming (a) the non-radical mechanism for the reaction S(IV) + Fe(III) (standard simulation), and (b) the radical mechanism. The values shown are average cloud water concentrations (M) and transformation rates (Ms⁻¹) on model day 3 at noon and at midnight. The averages are computed by integration over the depth of the cloud (250 to 400 m at noon, 187.5 to 400 m at midnight).

Under the high-sulfur conditions simulated here, the self-reaction is dominant:

\[(R7) \quad SO_2^+ + SO_2^- \rightarrow 2SO_4^- + O_2\]

The sulfate radical produced by (R7) reacts rapidly with most reduced species. Reaction with HSO_3^- would complete the propagation cycle:

\[(R8) \quad SO_4^- + HSO_3^- \rightarrow SO_3^- + H^+ + SO_2^2^-\]

However, Cl⁻ is more abundant than HSO_3^-, so that (R9) dominates over (R8):

\[(R9) \quad SO_4^- + Cl^- \rightarrow SO_2^- + Cl\]

\[(R10) \quad Cl^- + Cl^- \rightarrow Cl_2\]

Reaction (R9) produces the Cl/Cl_2 radical, which is mainly present as Cl_2 at the Cl⁻ concentrations simulated here. Reaction of Cl_2 with HSO_3^- would again complete the propagation cycle:

\[(R11) \quad HSO_3^- + Cl_2 \rightarrow SO_3^- + 2Cl^- + H^+\]

However, recent kinetic studies [Wine et al., 1988; McElroy, 1988] indicate that the reaction of Cl with H_2O is sufficiently fast to compete with (R11):

\[(R12) \quad Cl^- + H_2O \rightarrow Cl^- + H^+ + OH\]

Wine et al. [1988] report a preliminary rate constant of 1x10⁵ s⁻¹ for (R12); they find by contrast that the reaction Cl_2 + H_2O is very slow. Under our model conditions, the reaction Cl + H_2O effectively prevents propagation of the chain (Table 5). As a result the S(VI) yield is little more than unity, and the S(IV) + OH reaction is only a minor contributor to total S(VI) production.

Efficient propagation of the reaction chain could, however, occur at different HSO_3^- and Cl⁻ concentration regimes. From the mechanism of Table 5 we derive an analytical expression for the S(VI) yield as a function of droplet composition:

\[S(VI) \text{ yield} = \frac{1}{1 - A}\]  \hspace{1cm} (6)

with

\[A = \frac{k_{11}[HSO_3^-]}{k_{11}[HSO_3^-] + k_{12}[NO_3^-] + k_{13}[Cl^-] + k_{14}[Fe(II)] + k_{15}}\]

\[B = k_9[HSO_3^-] + k_{9}[Cl^-] + k_{13}[Mn(II)] + k_{14}[Fe(II)] + k_{15}\]

Fig. 15. Time evolution of simulated S(IV) and S(VI) concentrations in layer 1, assuming the radical mechanism for the S(IV) + Fe(III) reaction.
TABLE 5. Radical-assisted chain oxidation of S(IV)

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate, M s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initiation</td>
<td></td>
</tr>
<tr>
<td>(R5a) HMS + OH → SO₃⁻ + CH₂O + H₂O</td>
<td>1.4(-9)</td>
</tr>
<tr>
<td>(R5b) HSO₃⁻ + OH → SO₃⁻ + H₂O</td>
<td>1.2(-10)</td>
</tr>
<tr>
<td>(R5c) HAMS + OH → MGLYA + SO₃⁻ + H₂O</td>
<td>3.4(-11)</td>
</tr>
<tr>
<td>(R5d) GMBS + OH → GLYXXA + SO₃⁻ + H₂O</td>
<td>1.7(-11)</td>
</tr>
<tr>
<td>Propagation</td>
<td></td>
</tr>
<tr>
<td>(R6) SO₃⁻ + O₂ → SO₅⁻</td>
<td>8.3(-10)</td>
</tr>
<tr>
<td>(R7) SO₄²⁻ + SO₃⁻ → 2SO₂⁺ + O₂</td>
<td>8.3(-11)</td>
</tr>
<tr>
<td>(R8) SO₂ + HSO₃⁻ → SO₂⁺ + SO₅⁻ + H⁺</td>
<td>1.7(-9)</td>
</tr>
<tr>
<td>(R9) Cl⁻ + Cl₂⁻ → SO₂⁺</td>
<td>1.7(-9)</td>
</tr>
<tr>
<td>(R10) Cl⁻ + Cl₂⁻ = Cl₂⁻</td>
<td>1.7(-10)</td>
</tr>
<tr>
<td>(R11) HSO₃⁻ + Cl₂⁻ → SO₂⁺ + 2Cl⁻ + H⁺</td>
<td>7.6(-12)</td>
</tr>
</tbody>
</table>

Termination                                    |             |
| (R12) Cl⁻ + H₂O → Cl⁻ + H⁺ + OH                 | 1.5(-9)     |
| (R13) SO₂⁻ + Mn(II) → SO₂⁺ + Mn(III)            | 2.9(-11)    |
| (R14) SO₂⁻ + Fe(II) → SO₂⁺ + Fe(III)            | 2.6(-11)    |
| (R15) SO₂⁻ + H₂O → SO₂⁺ + H⁺ + OH               | 2.4(-11)    |
| (R16) Cl₂⁻ + NO₂⁻ → 2Cl⁻ + NO₂⁻                | 7.6(-12)    |

Rates are for 375 m AGL at noon. Read 1.4(-9) as 1.4x10⁻⁹.

where we have defined the S(VI) yield as the number of S(VI) molecules produced per individual reaction S(IV)+OH. The yield computed from equation (6) is plotted in Figure 16 as a function of [HSO₃⁻] and [Cl⁻], with concentrations of other species fixed at their values from the standard simulation. The yield increases linearly with [HSO₃⁻] for [HSO₃⁻] > 1 μM, but the dependence on [Cl⁻] is more complicated. In the limit of low [Cl⁻] the reaction SO₂⁻ + Cl⁻ is unimportant, and the yield is therefore independent of [Cl⁻]. As [Cl⁻] increases, the reaction SO₄⁻ + Cl⁺ becomes the major loss mechanism for SO₄⁻, leading to chain termination by the reaction Cl⁻ + H₂O. However, an increase of [Cl⁻] also decreases [Cl⁻] by shifting the Cl⁻/Cl₂⁻ equilibrium toward Cl₂⁻; eventually at high [Cl⁻], reaction (R11) dominates (R12), and the chain is efficiently propagated. A minimum in the S(VI) yield is found for [Cl⁻] of the order of 10⁻⁴ M. The conditions of the Bakersfield simulation happen to coincide with this minimum (Figure 16).

Inspection of Figure 16 suggests that high S(VI) yields could be achieved when [HSO₃⁻] > 10⁻³ M. Bisulfite concentrations of this magnitude require an unusual combination of high SO₂ concentration and high pH [Munger et al., 1984]. However, equation (6) relies on the assumption that HSO₃⁻ is the only S(IV) species involved in the chain-propagating reactions with SO₂ and Cl₂⁻; the S(VI) yields could be much higher if (S(IV)-carbonyl adducts were involved in chain propagation. For example, if we assume that all S(IV) species react with SO₂ and Cl₂⁻ at the same rate as HSO₃⁻ (and give identical sulfur radical products), then [S(IV)] should replace [HSO₃⁻] as the ordinate in Figure 16. Total S(IV) cloud water concentrations in excess of 10⁻³ M are observed routinely in polluted fogs and stratus clouds [Richards et al., 1983; Munger et al., 1984], so that high S(VI) yields would occur over a broad range of conditions. Another regime where high S(VI) yields would be expected is for [Cl⁻] > 10⁻³ M (Figure 16). Such Cl⁻ concentrations are commonly found in coastal fogs and stratus [Jacob et al., 1985; Munger, 1989] and have also been observed in highly polluted fogs near Zurich, Switzerland [Johnson et al., 1987].

5. DISCUSSION

5.1. Control of Sulfate Production by Ammonia

Table 6 summarizes the results from a number of sensitivity simulations in which we investigated the effects of changes in model conditions on model results. A remarkable feature common to all simulations is the close balance between concentrations of acids and bases; in all cases, the atmospheric alkalinites are small compared to the total concentrations of acids or bases. We also find that the predicted S(VI) concentrations are largely insensitive to changes in SO₂ emissions, NO₂ emissions, cloud liquid water content, or trace metal concentrations. By contrast they vary almost linearly with NH₃ emissions and are strongly dependent on the boundary layer ventilation rate.

It appears from Table 6 that the sensitivity of S(VI) concentrations to changes in model conditions reflects mainly the effect of these changes on the N(III) concentrations. The reason for this behavior is that S(VI) production by the S(IV) + Fe(III) reaction is controlled by the availability of NH₃. The S(IV) + Fe(III) reaction adds acidity to the droplet and is self-limiting unless NH₃ is available to neutralize the acidity; continuous supply of NH₃ from fresh emissions sustains a matching production of S(VI), but once NH₃ is exhausted, a small increase in S(VI) causes a rapid drop in cloud water pH which quenches further S(VI) production. The NH₃ concentrations simulated by the model (>1000 neq m⁻²) are much higher than the free acidities needed to quench the S(IV) + Fe(III) reaction in cloud (10-100 neq m⁻²), so that the total concentration of acids in cloud is only slightly in excess of the N(III) concentration. At ground level we find that N(III) is in slight excess (Table 6) because of the proximity of the NH₃ source.

![Fig. 16. Sulfate yield of the radical-assisted S(IV) oxidation chain as a function of [HSO₃⁻] and [Cl⁻], with other conditions as in Table 5. The yield is computed from equation (6). The dot indicates the conditions of the standard Bakersfield simulation.](image)
TABLE 6a. Summary of Results From Sensitivity Runs: Concentrations in Layer 1, Model Day 3 at Midnight

<table>
<thead>
<tr>
<th></th>
<th>S(VI)</th>
<th>S(IV)</th>
<th>N(V)</th>
<th>N(-III)</th>
<th>ALK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Observations</td>
<td>855</td>
<td>395</td>
<td>1196</td>
<td>-54±281</td>
<td></td>
</tr>
<tr>
<td>Standard model</td>
<td>771</td>
<td>26</td>
<td>347</td>
<td>1207</td>
<td>63</td>
</tr>
<tr>
<td>Liquid water content</td>
<td>735</td>
<td>10</td>
<td>380</td>
<td>1194</td>
<td>69</td>
</tr>
<tr>
<td>10% metals soluble</td>
<td>701</td>
<td>78</td>
<td>345</td>
<td>1196</td>
<td>72</td>
</tr>
<tr>
<td>No ventilation</td>
<td>1288</td>
<td>48</td>
<td>671</td>
<td>2070</td>
<td>63</td>
</tr>
<tr>
<td>SO₂ emissions/2</td>
<td>743</td>
<td>28</td>
<td>347</td>
<td>1187</td>
<td>69</td>
</tr>
<tr>
<td>NH₃ emissions/2</td>
<td>354</td>
<td>10</td>
<td>317</td>
<td>695</td>
<td>14</td>
</tr>
<tr>
<td>NO₂ emissions/2</td>
<td>840</td>
<td>28</td>
<td>266</td>
<td>1198</td>
<td>64</td>
</tr>
</tbody>
</table>

Concentrations are in units of neq m⁻³.

* Expected value ± uncertainty; the uncertainty on the measured value of (ALK) is large because the individual uncertainties on the measurements of (S(VI)), (N(V)), and (N(-III)) are compounded (see JMWH).

b As compared to 30% in the standard simulation.

It follows from the above discussion that a close balance between acids and bases should be a general characteristic of highly polluted atmospheres where aqueous-phase oxidation of SO₂ is the main source of acidity. Indeed, the fact that such a balance is systematically observed at Bakersfield can be taken as indirect evidence that the oxidation of SO₂ proceeds by an aqueous-phase mechanism whose rate decreases with decreasing pH. The frequently observed correlation between [SO₄²⁻] and [NH₄⁺] in precipitation over polluted regions [Schuurs et al., 1988] can also be explained in this manner. Control of S(VI) production by NH₃ may further explain the observation that S(VI) aerosol tends to be neutral in cities and acidic in rural environments [Koultrakis et al., 1988; P. Koultrakis, Harvard School of Public Health, personal communication, 1988].

5.2. Cloud Water pH

The cloud water pH at night is controlled by a balance between the reaction S(IV) + Fe(III) (which is the main source of acidity) and NH₃ emission. Because the rate of the S(IV) + Fe(III) reaction is strongly dependent on cloud water pH, a steady state pH is approached where the rate of acid production equals the rate of NH₃ emission. An approximate analytical expression for this steady state can be obtained using a simplified box model with the following assumptions: (1) the cloud is of uniform composition, (2) transport within the boundary layer is rapid, and (3) SO₂ levels are controlled by emission and deposition. The balance between S(VI) production and NH₃ emission is then expressed as follows:

\[
\frac{2kK_HK_{\text{Fe}}K_{\text{S}}RT}{V_d[H^+]^{1/2}} \frac{(\text{Fe}(\text{III}))E_{\text{SO₂}}}{E_{\text{NH₃}}} = \frac{E_{\text{SO₂}}}{2T}
\]

where \(k(M^{-1} s^{-1})\) is the aqueous-phase rate constant of the S(IV) + Fe(III) reaction; \(K_H(M \text{ atm}^{-1})\), \(K_{\text{Fe}}(M)\), and \(K_{\text{S}}(M)\) are the Henry's law and acid dissociation constants for SO₂; \(R\) (atm cm² mol⁻¹ K⁻¹) is the ideal gas constant; \(T\) (degrees Kelvin) is the temperature; \(V_d\) (centimeters per second) is the SO₂ deposition velocity; \((\text{Fe}(\text{III}))\) is the Fe(III) concentration in moles per cubic centimeter of air; \(E_{\text{NH₃}}\) and \(E_{\text{SO₂}}\) (molecules per square centimeter per second) are emission rates of NH₃ and SO₂, respectively; and \(z_T\) (centimeters) is the thickness of the boundary layer. Rearrangement of equation (7) yields an expression for the steady state \([H^+]:\)

\[
[H^+] = \left[ \frac{2kK_HK_{\text{Fe}}K_{\text{S}}RTz_T}{V_d} \frac{(\text{Fe}(\text{III}))E_{\text{SO₂}}}{E_{\text{NH₃}}} \right]^{1/2}
\]

The dependence of \([H^+]\) on \(E_{\text{SO₂}}/E_{\text{NH₃}}\)² in equation (8) implies that the cloud water pH should be only moderately sensitive
changes in emissions of NH₃, SO₂, or NOₓ directly alter the magnitude of the excess acidity and thus have a strong effect on cloud water pH. Variations in cloud liquid water content also affect pH in the daytime by changing the amount of water into which the excess acidity is dissolved. The radiation field plays an important role in determining the daytime acid production rates because the OH concentrations scale almost linearly to the radiation intensities. Accurate representation of the radiation field in and below cloud is therefore a critical element in the simulation of acid production in polluted cloudy boundary layers.

6. Conclusions

We have developed a detailed photochemical model which simulates successfully the main features of the chemical evolution observed during a wintertime stagnation episode with low stratus in Bakersfield, California. A remarkable feature of the observations is the close balance maintained at all times between total atmospheric concentrations of acids and bases. We argue that this balance is evidence that the production of H₂SO₄ (the principal contributor to the acidity) proceeds by an aqueous-phase SO₂ oxidation mechanism whose rate is inversely dependent on droplet acidity. The only mechanism in the model that provides a source of sulfate consistent with the observed sulfate accumulation pattern is the S(IV) + Fe(III) reaction, assuming that this reaction proceeds by a non radical mechanism in which Fe(III) acts as a catalyst for the autoxidation of S(IV). A radical mechanism for the S(IV) + Fe(III) reaction with Fe(II) and SO₂ as intermediate products is found to quench S(IV) oxidation because of depletion of Fe(III); this result follows from the absence of a rapid Fe(II) oxidation pathway in the model. The radical mechanism could possibly be an efficient source of sulfate if Fe(II) were oxidized to Fe(III) by a pathway not included in the model, e.g. the S(IV)-induced autoxidation reaction [Faust, 1985], or bacterial oxidation. Such pathways remain, however, hypothetical at this time. More laboratory studies of the mechanism of the S(IV) + Fe(III) reaction are needed.

Other aqueous-phase S(IV) oxidation mechanisms with rates inversely dependent on droplet acidity include the reactions with O₃ and OH. Very low concentrations of O₃ are observed in Bakersfield during wintertime stagnation episodes; therefore the S(IV) + O₃ reaction is negligible. The S(IV) + OH reaction initiates a S(IV) oxidation chain which would be a major source of sulfate if efficiently propagated. However, we find that chain propagation does not occur under our simulated conditions because of rapid termination by the reaction SO₂ + Cl⁻ followed by Cl + H₂O. Efficient propagation could take place under high-SO₂ conditions if the S(IV)-carbonyl adducts participate in the chain propagation steps, and also under high-Cl⁻ conditions (as in coastal fog and stratus). The model results point to the need for further kinetic information on the hydrolysis reactions of Cl and Cl₂, and for kinetic and product information on the reactions of S(IV)-carbonyl adducts with radical oxidants.

The inverse dependence of aqueous-phase SO₂ oxidation on cloud water acidity implies that sulfate production in the Bakersfield atmosphere (and in similar highly polluted environments) should be largely independent of SO₂ emissions and increase linearly with NH₃ emissions. Extremely high cloud water acidities (pH < 3) are unlikely to occur in such environments as a result of aqueous-phase SO₂ oxidation. High acidities may, however, be attained by other mechanisms, e.g., photochemical gas-phase acid production by the reactions NO₂ + OH and SO₂ + OH.

Fig. 18. Gas-phase production of acidity as a function of time of day on model day 3. Results are shown as column rates integrated over the depth of the boundary layer. The solid line is the total acid production rate from the reactions NO₂ + OH and SO₂ + OH (the latter reaction produces two equivalents of acidity). The dashed line is the contribution from NO₂ + OH alone. The dotted line is the NH₃ emission rate.

The lower pH values in the daytime than at night are due to additional acid input from the photochemical gas-phase reactions NO₂ + OH and SO₂ + OH. We plot in Figure 18 the gas-phase acid production rate integrated over the depth of the boundary layer, in the standard simulation, as a function of time of day; the diurnal variation of this rate essentially follows that of the OH concentration. As long as NH₃ emissions (superimposed on Figure 18 for comparison) exceed the gas-phase acid production rate, the cloud water pH can still be described approximately by a steady state between the reaction S(IV) + Fe(III) and the available excess NH₃. This steady state pH decreases as the morning progresses and NH₃ is increasingly depleted by the growing acid input. Eventually at midday the gas-phase acid production rate exceeds the rate of NH₃ emissions, and acidity accumulates in the boundary layer, causing a rapid pH drop, particularly in the bottom portion of the cloud where the liquid water content is lowest (Figure 9). This regime of excess acid production is maintained only for about 2 hours, until 1330 local time; at that time the cloud water pH has reached its minimum value and begins to rise again in response to the excess input of NH₃. By late afternoon the cloud water pH is back at a value approaching the nighttime steady state.

From the above discussion it appears that extremely high acidities in the Bakersfield atmosphere may be attained only during the daytime hours when gas-phase acid production by the reactions NO₂ + OH and SO₂ + OH exceeds NH₃ emissions. The cloud water acidities predicted by the model in the daytime are more sensitive to model conditions than at night, as shown in Table 6;
### TABLE A1. Optical Properties of the Cloud

<table>
<thead>
<tr>
<th>Wavelength, nm</th>
<th>310</th>
<th>400</th>
<th>600</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photolysis</td>
<td>O₃→O(¹D)</td>
<td>NO₂</td>
<td>O₃ (Chappuis)</td>
</tr>
<tr>
<td>Mie</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Qₑ</td>
<td>2.062</td>
<td>2.077</td>
<td>2.097</td>
</tr>
<tr>
<td>Qₑ*</td>
<td>1.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ω</td>
<td>0.999993</td>
<td>0.999999</td>
<td>0.999998</td>
</tr>
<tr>
<td>Atmosphere</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>τ(Raleigh)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Above cloud</td>
<td>0.90</td>
<td>0.27</td>
<td>0.054</td>
</tr>
<tr>
<td>Below cloud</td>
<td>0.10</td>
<td>0.03</td>
<td>0.006</td>
</tr>
<tr>
<td>τ(stratospheric ozone)</td>
<td>[0,1]</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>τ(cloud)</td>
<td>[0.1,2,4,8,16]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ω</td>
<td>[0.98,1.00]</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

Brackets denote the set of different values for the cases.

### APPENDIX: PHOTOLYSIS IN THE PRESENCE OF CLOUD

**A1. Introduction**

A new method of solving for the radiation field in an inhomogeneous, plane-parallel atmosphere with anisotropic scattering is presented. The technique is applicable to stratocumulus clouds. It is based on the multistream method of Feautrier [1964] which has been extended to polarized Rayleigh scattering [Prather, 1974] and to anisotropic scattering by L. H. Auer and M. J. Prather (unpublished, see applications by Cochran and Trajfan [1978] and Logan et al. [1981]). In this appendix we describe the physical properties of the cloud and relate them to the optical properties. The Mie phase function for the cloud is compared with the Henyey-Greenstein phase function. The method of solution is documented, and results for several atmospheric cases are presented.

**A2. Physical Properties of the Cloud**

The cloud is assumed to be a polydispersed gamma distribution n(r) of spheres of pure H₂O with an effective radius a = 10 μm. We define X (units per cubic meter) to be the total concentration of drops, G (square meters) to be the average geometric cross section per droplet, and V (m³/m³) to be the fractional volume occupied by the drops. The equations relating these quantities are then

\[
\frac{d\ln[n(r)]}{d\ln[r]} = \frac{1}{b} - \frac{3}{ab} \quad (A1)
\]

where \( r \) is the droplet radius, \( b = 0.15 \) is a constant, and

\[
X = \int_0^\infty n(r) \, dr \quad (A2a)
\]

\[
G = \frac{\pi r^2 n(r) \, dr}{X} = 1.87 \times 10^{-10} \text{ m}^2 \quad (A2b)
\]

\[
V = \frac{(4/3) \pi}{G} \quad (A2c)
\]

This distribution of drop sizes is typical of water clouds and gives a Mie scattering function that is moderately uniform with wavelength [see Dzmitrowicz, 1969]. The vertically integrated geometric cross section \( A \) of the cloud (dimensionless) is given by

\[
A = \int_0^\infty G X \, dz = \frac{3 \times 10^{-6}}{4a} \int_0^\infty W \, dz \quad (A3)
\]

where \( W \) is the liquid water content in grams of liquid water per cubic meter of air \( (W = 10^4 \text{g}) \). In the Bakersfield simulation the total liquid water column in the daytime is 24 g m⁻²; hence the vertically integrated geometric cross section is 1.8.

**A3. Optical Properties of the Cloud**

The optical properties of the cloud depend on wavelength and are derived from the distribution of droplet sizes and Mie scattering theory for spheres of pure H₂O [Hansen and Travis, 1974]. We use the Mie phase function for scattering of natural light, assuming that all light is unpolarized. A more complete treatment of scattering including polarization is not necessary for these conditions [Prather, 1974]. The cloud is assumed to be homogeneous and may therefore be described optically by a total extinction optical depth \( \tau_{ex} \) (dimensionless), a single scattering albedo \( \omega \), and a scattering phase function \( P \).

The optical depth for extinction (absorption plus scattering) of light is related to the geometric cross section by the efficiency factor \( Q_{ex} \) derived from Mie theory,

\[
\tau_{ex} = Q_{ex} \ A \quad (A4)
\]

The factor \( Q_{ex} \) is approximately 2 for the combination of droplet sizes and wavelengths considered here and does not vary much over the wavelength range 300-600 nm, as shown in Table A1.

The single scattering albedo \( \omega \) describes which fraction of extinction events results in scattering rather than absorption. For the visible wavelengths, water does not absorb significantly, less than 1 event in 10⁴; and thus \( \omega \) may be approximated as unity for clouds of modest optical depth.

The phase function \( P(\cos \theta) \) defines the probability that scattered light will be deflected by an angle \( \theta \) from its incident direction. The value of \( P \) is normalized such that integration over all solid angles \( (4\pi \text{sr}) \) is unity.

\[
\frac{1}{2} \sum_{-\infty}^{\infty} P(\cos \theta) \sin \theta \, d\theta = 1 \quad (A5)
\]
Mie phase functions for scattering of natural light are shown in Figure A1. From 300 to 600 nm, differences with wavelength are modest. The peaks in the phase functions correspond to the glory (180°), primary and secondary rainbows (142° and 122°), and the forward peak (0°, shown on an expanded scale in Figure A1b [see van de Hulst, 1981]). This forward peak is the most difficult part of the Mie phase function to model: it includes an extremely nonlinear response at small θ that is basically a diffraction pattern. For example, a black disk has an extinction efficiency Qₑ = 2, with absorption comprising half (ω = 0.5) and scattering described by the diffraction pattern.

Anisotropic scattering by small particles is often approximated by the analytic Henyey-Greenstein phase function,

$$ P_{HG}(\cos \theta) = \frac{1 - g^2}{(1 + g^2 - 2g \cos \theta)^{3/2}} \quad (A6) $$

where the parameter g is a measure of the anisotropic forward peak. A comparison is made between a family of $P_{HG}$ phase functions ($g = 0.8$ to 0.995) and $P_{MIE}$ in Figure A2. While the Henyey-Greenstein phase function captures the essence of forward scattering, it does not adequately represent the shape of the Mie phase function.

Our solution of the scattering problem requires that the Mie phase function $P_{MIE}(\cos \theta)$ be decomposed into a Legendre series, but the forward diffraction peak cannot be adequately represented by an expansion of orthogonal polynomials in $\cos \theta$. The forward peak results in very small scattering angles and may be treated as having merely passed the light through without scattering. Therefore we choose to truncate this forward peak by extrapolating $\log(P_{MIE})$ linearly in $\cos \theta$ from 1° to 0°. This revised phase function is expanded in a Legendre series out to 80 terms and given in Table A2. The resulting phase functions—true Mie, truncated Mie, Legendre expansion—are compared in Figures A3 and A4 for the wavelength 400 nm. The Legendre expansion accurately reproduces the truncated Mie function to better than $10^5$ for the range of $P$ from $10^{-2}$ to $10^1$, with the exception of the glory (not truncated like the forward peak) where errors are as large as $10^{-0.18}$.

Truncation of the forward peak reduces the effective scattering cross section and leads to a phase function that is not correctly normalized. The renormalized phase function $P^*$ results in a value of $Q_{ex}$ close to unity (see Table A1). Thus the cloud in the Bakersfield simulation has a renormalized extinction optical depth $\tau_{ex}$ equal to approximately 2 rather than 4. In the following we assume that all optical parameters have been renormalized and drop the asterisk notation.

**A.4. Solution of the Equation of Radiative Transfer**

We present in this paper a new method of solving for anisotropic scattering by separating the even and odd parts of the radiation field and by solving the pair of differential equations that couple them. The equation of radiative transfer is solved for all orders of scattering in its integro differential form [Chandrasekhar, 1960]

$$ \frac{dI(\tau, \mu, \phi)}{d\tau} = I(\tau, \mu, \phi) \\
- \frac{\alpha(\tau)}{4\pi} \int d\phi' P(\tau, \mu, \phi, \mu', \phi') I(\tau, \mu', \phi') \\
- P(\tau, \mu, \phi, \mu, \phi) \pi F e^{-\tau_{ex}} \quad (A7) $$

In this notation, $I(\tau, \mu, \phi)$ is the specific intensity (photons cm$^{-2}$ s$^{-1}$ sr$^{-1}$) in the direction $(\mu, \phi)$; the direction $(\mu, \phi)$ refers to the cosine of the zenith angle (e.g., $\mu = +1$ points upward) and the azimuthal angle, respectively; $\tau$ is the vertical optical depth, nominally zero at the top of the atmosphere; $\omega$ is the single scattering albedo; $P(\tau, \mu, \phi, \mu', \phi')$ is the phase function at optical depth $\tau$ for scattering by an angle

$$ \cos \theta = \mu \mu' + (1-\mu^2)1/2 (1-\mu'^2)1/2 \cos(\phi - \phi') \quad (A8) $$

Fig. A2. Phase function for scattering of spheres of pure H$_2$O with a gamma distribution of effective radius 10 $\mu$m. The value of $\log P$ is plotted as a function of the cosine of the scattering angle. The Mie phase function at 400 nm is compared to a family of Henyey-Greenstein phase functions ($g = 0.8$ to 0.995).
and \( \pi F_\phi \) is the flux incident on the top of the atmosphere in the direction \((-\mu, \phi_0)\).

The decomposition of equation (A.7) into Fourier components follows Chandrasekhar [1960, pp. 149–150]. The phase function times the single scattering albedo is expressed as a finite series of \(L+1\) Legendre polynomials, \(P_l\), where the coefficients \(\omega_l\) are functions of \(\tau\), and \(\omega_l(\tau) = \omega(\tau)\).

\[
\omega(\tau)P(\tau, \cos \theta) = \sum_{l=0}^{L} \omega_l(\tau)P_l(\cos \theta)
\]  

where \(P_l^m\) are the renormalized associated Legendre functions [Dave and Armstrong, 1970] and \(I_l^m = P_l\). When the specific intensity is expanded similarly with respect to the solar azimuth angle \(\phi_0\),

\[
I(\tau, \mu, \phi) = \sum_{m=0}^{L} I_l^m(\tau, \mu) \cos m(\phi - \phi_0) \tag{A11}
\]

we have the equation for the zeroth moment,

\[
\mu \frac{dP(\tau, \mu)}{d\tau} = \mu P(\tau, \mu) - \frac{1}{2} \sum_{l=0}^{L} \omega_l(\tau)P_l(\mu) \int \mu' P_l(\mu') P^m(\tau, \mu') d\mu' \tag{A12}
\]

and \(L\) additional independent equations, \(m = 1 \text{ to } L\), for components of the radiation field that are periodic in \((\phi, \phi_0)\).

For this paper we are interested in the radiation field contributing to the photolysis rates,

\[
J(\tau) = \pi F_\phi e^{-\mu_0} + 4\pi <I(\tau)> \tag{A14}
\]

where the mean intensity \(<I>\) depends only on the zenith order of the specific intensity,

\[
<I(\tau)> = \frac{1}{4\pi} \int \int d\mu d\phi I(\tau, \mu, \phi) = \frac{1}{2} \int \mu P(\tau, \mu) \tag{A15}
\]

The method of solution for \(P\) is described below (dropping the superscript zero notation). Solutions for higher orders of \(I\) are needed only if the azimuthal dependence of the radiation field is needed (e.g., to compare with observations) and can be performed in a similar manner.

The odd-even symmetry of the Legendre functions, \(Y_l^m(\mu) = (-1)^{m-l}Y_l^m(\mu)\), can be used to derive separate, but coupled equations for \(J(\tau, \mu)\) and \(H(\tau, \mu)\) defined as

\[
J(\tau, \mu) = \frac{1}{2} [I(\tau, +\mu) + I(\tau, -\mu)] \tag{A16}
\]

\[
H(\tau, \mu) = \frac{1}{2} [I(\tau, +\mu) - I(\tau, -\mu)] \tag{A17}
\]

with \(0 < \mu < 1\). The integrals can be expressed in terms of \(J\) and \(H\) by noting that

\[
\int_{-1}^{1} I(\tau, \mu) P_l(\mu) d\mu = 2 \int_{-1}^{0} J(\tau, \mu) P_l(\mu) d\mu \quad \text{gcd even} \tag{A18}
\]

\[
\int_{-1}^{1} I(\tau, \mu) P_l(\mu) d\mu = 2 \int_{-1}^{0} H(\tau, \mu) P_l(\mu) d\mu \quad \text{odd} \tag{A19}
\]
the integrals over the cosine of the zenith angle in equations (A20) and (A21) are approximated by Gaussian quadrature, e.g.,

$$
\int_0^1 P_i(\mu) j(\tau, \mu) d\mu = \sum_{k=1}^K w_k P_i(\mu_k) j(\tau, \mu_k)
$$

(A22)

For the Mie functions expanded to $P_9$ we use $K = 40$, which is the minimum number of quadrature angles necessary for $L = 79$. For the $\tau$ grid, $\tau_1 = 0$ is chosen as the top of the atmosphere, and $\tau_N$ at the bottom of the atmosphere is the total optical depth. We use $j_{\mu}$ and $h_{\mu}$ to denote $j(\tau, \mu)$ and $k(\tau, \mu)$, respectively.

Regarding the coupled equations (A20) and (A21), note that the first derivative of $j$ is a function only of $h$, and vice versa. For the case of isotropic or Rayleigh scattering [e.g., Prather, 1974] the odd terms $\Sigma^{2d}$ vanish and the pair of equations (A20) and (A21) can be readily collapsed into a single second-order differential equation involving only $j$ and $d^2 j/d\tau^2$. This second-order ordinary differential equation would be solved by using finite differences over a $\tau$ grid with second-order boundary conditions [Auer, 1967].

The innovative approach used here to solve the asymmetric scattering problem is to recognize that we can calculate $j$ and $dh/d\tau$ at odd grid points, and $h$ and $dj/d\tau$ at the alternating even grid points. Requiring $N$ to be odd, there are $N-2$ equations of the following type for each interior grid point,

$$
k = 1, K
$$

$$
\frac{dj}{d\tau}\bigg|_{\tau_k} = \frac{j_{\mu} - j_{\mu_k}}{\tau_{\mu_k} - \tau_k} \quad \quad (A23)
$$

$$
\frac{dh}{d\tau}\bigg|_{\tau_k} = \frac{h_{\mu} - h_{\mu_k}}{\tau_{\mu_k} - \tau_k} \quad \quad (A24)
$$

where $[dj/d\tau]_{\mu_k}$ is equated to a linear combination of $h_{\mu_k}$ ($k' = 1, K$) and $[dh/d\tau]_{\mu_k}$ to a linear combination of $j_{\mu_k}$. For the boundary conditions we need two equations coupling $j$ at the boundary with $h$ at the adjacent interior point. At the upper boundary a first-order Taylor expansion is applied

$$
h_{\mu_k} = h_{\mu_k} + \frac{dh}{d\tau}\bigg|_{\tau_k} (\mu_{\mu_k} - \tau_k) + \text{second-order terms} \quad \quad (A25)
$$

The first derivative in equation (A25) is expressed as a linear combination of $j_{\mu_k}$ using equation (A21), and we substitute $j_{\mu_k} = h_{\mu_k}$ because there is no diffuse radiation incident on the top of the atmosphere (i.e., $I(\tau=0, \mu) = 0$). At the lower boundary a similar expansion is used,

$$
\begin{align*}
\frac{dj}{d\tau}\bigg|_{\tau_k} &= \frac{j_{\mu} - j_{\mu_k}}{\tau_{\mu_k} - \tau_k} \\
\frac{dh}{d\tau}\bigg|_{\tau_k} &= \frac{h_{\mu} - h_{\mu_k}}{\tau_{\mu_k} - \tau_k}
\end{align*}
$$

Fig. A3. Phase function for scattering of spheres of pure H$_2$O with a gamma distribution of effective radius 10 $\mu$m. The value of log $P$ is plotted as a function of the cosine of the scattering angle. The Mie phase function at 400 nm (MIE) is compared to the truncated Mie phase function (MIE/T) and to the Legendre expansion of the truncated Mie phase function (L79/T). (a) The full scale. (b) An expanded scale about the forward peak.

Let $\Sigma^{2d}$ denote the sum over all odd-numbered Legendre polynomials beginning with $P_1$, and $\Sigma^{2e}$ the sum over even polynomials beginning with $P_0$. Then we may derive a pair of coupled differential equations for $j$ and $h$ over the domain $0 < \mu < 1$.

$$
\frac{dj}{d\tau} = \frac{1}{2} \left[ (\mu) \frac{dP_i(\mu)}{d\tau} + (\mu) \frac{dP_i(\mu)}{d\tau} \right] \\
= h(\tau, \mu) - \Sigma^{2d} \omega P_i(\mu) P_i(\mu') h(\tau, \mu') d\mu' \\
- \frac{1}{2} F_0 e^{-\nu \omega} \Sigma^{2d} \omega P_i(\mu) P_i(\mu') d\mu'
$$

(A20)

$$
\frac{dh}{d\tau} = \frac{1}{2} \left[ (\mu) \frac{dP_i(\mu)}{d\tau} - (\mu) \frac{dP_i(\mu)}{d\tau} \right] \\
= j(\tau, \mu) - \Sigma^{2e} \omega P_i(\mu) P_i(\mu') j(\tau, \mu') d\mu' \\
- \frac{1}{2} F_0 e^{-\nu \omega} \Sigma^{2e} \omega P_i(\mu) P_i(\mu') d\mu'
$$

(A21)

We solve for $j(\tau, \mu)$ and $h(\tau, \mu)$ at a discrete set of angle points $(\mu_k$, $k = 1, K)$ and over a discrete grid of optical depth $(\tau_i$, $i = 1, N)$. The set of angle points are chosen to be the Gaussian quadrature points $(\mu_k)$ with associated weights $(\omega_k)$ over the interval $0 < \mu < 1$. Then

Fig. A4. Comparison of the Legendre expansion at 400 nm ($P$) to the truncated Mie phase function ($P_{MIE}$). The logarithm of the ratio is plotted as a function of the cosine of the scattering angle.
Fig. A5. Monochromatic $J$ values normalized to the reference value $\pi F_0$, as a function of altitude. A cloud of renormalized optical thickness $\tau_{\text{ext}} = 4$ is embedded between altitudes 500 m and 1000 m. The ground reflectivity is 0.1. Results are shown for three different wavelengths (310, 400, and 600 nm) and two solar zenith angles, (a) $\mu_o = 1$ and (b) $\mu_o = 0.25$. Results at 310 nm are shown both with and without absorption from stratospheric ozone (plots 310s and 310, respectively).

$$h_{N-1,A} = h_{N\lambda} - \left[ \frac{dh}{dt} \right]_{h_{N\lambda}}(\tau_{\text{ext}}) + \text{second–order terms} \tag{A26}$$

but the relationship between $h_{N\lambda}$ and $j_{N\lambda}$ is more complex. The lower boundary is assumed to be Lambertian, that is, the specific intensity reflected from the surface is isotropic ($I(\tau_{\text{ext}}) = I_{\lambda}$) with a hemispheric flux equal to a fraction ($\lambda$) of the flux incident on the lower boundary. The equations are

$$h_{N\lambda} = I_{\lambda} - j_{N\lambda} \tag{A27}$$

and

$$I_{\lambda} = \frac{4\lambda}{1 + \lambda} \int_{0}^{1} j_{\mu}(\mu) \mu d\mu = \frac{4\lambda}{1 + \lambda} \sum_{k=1}^{K} j_{\mu_k} \mu_k a_k \tag{A28}$$

(An alternate lower boundary condition may be applied in an optically thick atmosphere for which the radiation field can be considered symmetric in $\mu$: $h_{N\lambda} = 0$.) For the higher-order moments of the radiation field ($I_m, m = 1, L$) a Lambertian surface is black, $\lambda = 0$.

The NxKxN system of linear equations is efficiently solved as a block tri-diagonal system of equations with KxK blocks [Feautrier, 1964]. Results from the forward pass through the system can be saved and used to recompute the solution for a different right-hand side at negligible increase in computation (i.e., different solar zenith angles). The right-hand side involves only terms proportional to $F_0$ and the entire solution is, of course, linear in $F_0$. An obvious consequence of this linearity is that the average scattered intensity over a day can be derived with a single calculation by first averaging the source term, including the angular dependence in terms such as $P(\mu)P(-\mu)$. The computational time on an IBM 4381-13 is 49 seconds for the cases shown here (only $I_0, K = 40, N = 123$) including 7 different solar zenith angles.

A 5. The Radiation Field with a Stratus Cloud

The above solutions have been applied to a stratuslike cloud in the boundary layer. The monochromatic $J$ values, defined as $J/\pi F_0$ from equation (A14), are shown as a function of altitude for a variety of conditions in Figures A5-A9. The optical properties have been described above, and the calculations embed the cloud between altitudes 500 m and 1000 m in a Rayleigh scattering medium. The optical properties of the cloud are taken from the Mie calculations at 400 nm for all three wavelengths: 310, 400 and 600 nm.

Fig. A6. Monochromatic $J$ values at 400 nm normalized to the reference value $\pi F_0$, as a function of altitude. A cloud of renormalized optical thickness $\tau_{\text{ext}} = 2$ is embedded between altitudes 500 m and 1000 m. The ground reflectivity is 0.1. Results are shown for seven values of the zenith angle, ranging from $\mu_o = 0.06$ to $\mu_o = 1$.

Fig. A7. Monochromatic $J$ values at 400 nm normalized to the reference value $\pi F_0$, as a function of altitude. A cloud of renormalized optical thickness $\tau_{\text{ext}} = 1$ is embedded between altitudes 500 m and 1000 m. The ground reflectivity is 0.1, and $\mu_o = 1$. Results are shown for six values of $\tau_{\text{ext}}$ ranging from 0.1 to 16.
TABLE A3. J values in a Cloudy Atmosphere

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At 400 nm

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</table>

J values are normalized to the solar flux. The cloud is located between 500 and 1000 m, with
renormalized optical thickness of 2, single scattering albedo of 1, surface reflectivity (Lambertian)
of 0.1, and absorption by stratospheric ozone with optical depth 1 at 310 nm.

Figure A5 compares the J values as a function of wavelength for two solar zenith angles, \( \mu_o = 1 \) and 0.25. Major differences with wavelength are due to the amount of Rayleigh scattering above the cloud and to the inclusion of stratospheric ozone absorp-
tion at 310 nm. (Ozone absorption at 600 nm by the Chappuis bands, \( \tau = 0.04 \), would be negligible except at very small solar zenith angles and is not included.) All wavelengths show enhancements within and above the cloud. At 600 nm the atmosphere is almost transparent, and the J value maximizes within the cloud. The pair of calculations at 310 nm shows that stratospheric absorption tends to scale the results by \( e^{-1.5 \mu_o} \).

Figure A6 shows how the J values depend on solar zenith angle for the standard cloud case at 400 nm. The J value above the cloud changes only slowly with zenith angle for \( \mu_o > 0.5 \), but the radiation field in the bottom half of the cloud and near the ground decreases rapidly, almost linearly, with \( \mu_o \).

Figure A7 demonstrates the dependence of J values on the optical depth of the cloud at 400 nm for \( \mu_o = 1 \). As the optical thickness of the cloud increases above 1, the J value in the top half of the cloud increases almost logarithmically with optical depth, while that in the lower half decreases by about the same proportion. Similar calculations at 310 nm for \( \mu_o = 0.6 \), and with no absorption from stratospheric ozone, are shown in Figure A8. The basic response to solar zenith angle is similar to Figure A7.

Figure A9 takes the case from Figure A8 with optical depth equal to 4 and compares with three special cases. An increase in the ground reflectivity from 0.1 to 0.3 leads to a 40% increase in J values at the lower boundary of the cloud, but only a 6% increase at the top. A reduction in the single scattering albedo from 1 to

Fig. A8. Monochromatic J values at 310 nm normalized to the reference value \( \tau F_o \), as a function of altitude. A cloud of renormalized optical thickness \( \tau^* o \) is embedded between altitudes 500 m and 1000 m. The ground reflectivity is 0.1, and \( \mu_o = 0.6 \). Absorption by stratospheric ozone is not included. Results are shown for five values of \( \tau^* o \) ranging from 0.1 to 16.
Fig. A9. Monochromatic $J$ values at 310 nm normalized to the reference value $nFo$, as a function of altitude. A cloud of renormalized optical thickness $\tau_{eso} = 4$ is embedded between altitudes 500 m and 1000 m. In the standard case (squares) the ground reflectivity is 0.1, $\mu_o = 0.6$, the single scattering albedo is 1, and no absorption by stratospheric ozone is included. Results are shown for the effects of increased ground reflectivity from 0.1 to 0.3 (number signs), decreased single scattering albedo from 1 to 0.98 (inverted triangles), and absorption by stratospheric ozone (crosses).

0.98 results in about 10-20% reduction to the $J$ values increasing from top to bottom of the cloud. Including the absorption by stratospheric ozone greatly reduces the $J$ values, by almost a uniform scaling factor of 0.18 - $e^{-1.98\tau}$. Results from the two standard cases used in the photochemical model are given in Table A3. These tables give monochromatic $J$ values, $J/nFo$, throughout the troposphere as a function of altitude and cosine of the solar zenith angle. Rayleigh scattering is included as outlined in Table A1 and the ground reflectivity is assumed to be 0.1 (Lambertian). Ozone absorption is included at 310 nm and determines the strong falloff with zenith angle at this wavelength.

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REFERENCES


