

# Mathematical analysis of the stratospheric photochemical system

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[1] The impact of odd chlorine ( $\text{Cl}_y$ ) and odd nitrogen ( $\text{NO}_y$ ) perturbations (resulting from human activities) and of enhanced  $\text{H}_2\text{O}$ - $\text{H}_2\text{SO}_4$  aerosol load (associated with volcanic activity) on stratospheric ozone (25 km altitude, midlatitudes) is assessed by using a chemical box model in which key heterogeneous reactions on the surface of sulfate aerosol particles are taken into account. The model shows that if transport is ignored, the response of the photochemical system to increased abundances of odd chlorine and odd nitrogen and to enhanced aerosol surface area density is characterized by a multiequilibrium regime. Catastrophic transitions may occur and may produce dramatic reductions in the stratospheric ozone concentration. When the dissipative effects associated with transport are taken into account, the system still exhibits a nonlinear response to external nitrogen and chlorine sources but without multiequilibrium solutions or catastrophic transitions. Over a sensitive interval, small external disturbances applied to model parameters can lead to large changes in the state of the system. For example, the large drop in ozone derived by the model when dissipative transport effects are taken into account corresponds to a degeneracy of the multiequilibrium regime found when dissipative terms are omitted.

*INDEX TERMS:* 0317 Atmospheric Composition and Structure: Chemical kinetic and photochemical properties; 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0340 Atmospheric Composition and Structure: Middle atmosphere—composition and chemistry; 0341 Atmospheric Composition and Structure: Middle atmosphere—constituent transport and chemistry (3334); *KEYWORDS:* ozone, aerosol heterogeneous chemistry, nonlinear system, multiequilibrium, catastrophe

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## 1. Introduction

[2] Chemical reactions in the atmosphere are nonlinear processes. Over the last decades, various mathematical analyses of chemical systems [Prather *et al.*, 1979; Fox *et al.*, 1982; Cicerone *et al.*, 1983; White and Dietz, 1984; Kasting and Ackerman, 1985; Stewart, 1993; Yang and Brasseur, 1994, 2001; Hess and Madronich, 1997; Montecinos and Felmer, 1999] have revealed that the chemical composition of the troposphere and stratosphere could exhibit unexpected behavior and abrupt changes in response to external forcing. Prather *et al.* [1979], for example, showed that the equations describing chemical partitioning between the nitrogen, chlorine, and hydrogen species may admit multiple, physically reasonable solutions with abrupt changes to be expected at high latitudes during wintertime. Fox *et al.* [1982] showed that two of the solutions characterized by low- and high-ClO concentrations are stable

to infinitesimal perturbations and that under most conditions the high-ClO, low- $\text{NO}_2$  solution is the most stable solution.

[3] In a recent paper, Yang and Brasseur [2001] assessed the conditions under which catastrophic transitions could affect the stratospheric photochemical system in response to enhanced atmospheric abundances of reactive nitrogen and chlorine. Using a zero-dimensional box model accounting for the most important gas phase reactions occurring in the stratosphere (25 km altitude) at midlatitudes and ignoring transport processes, they showed that an abrupt transition in the concentration of chemical compounds with a catastrophic reduction in the ozone abundance could occur when the stratospheric source of nitrogen oxides becomes 2–3 times larger than the current production rate. They also indicated that as the atmospheric level of reactive chlorine increases (as a result, e.g., of increasing emissions of industrially manufactured chlorofluorocarbons), the system could shift from its original equilibrium state to a stable periodic state (periodic attractor) after encountering a supercritical Hopf bifurcation. This periodic behavior, which appears when the source of reactive chlorine becomes larger than approximately 10 times its current value, is characterized by a large-amplitude

**Table 1.** Model Parameters at 25 km Altitude

Parameter	Value
Temperature	220 K
Air number density	$8.24 \times 10^{17} \text{ cm}^{-3}$
O <sub>2</sub> number density	$1.73 \times 10^{17} \text{ cm}^{-3}$ (0.21%)
H <sub>2</sub> O number density	$2.74 \times 10^{12} \text{ cm}^{-3}$ (3.3 ppmv)
Photolysis	calculated at 40°N for equinox conditions (24 hour average)
Reaction probability for ClONO <sub>2</sub> hydrolysis on sulfate aerosols (72.7 wt %)	$2.65 \times 10^{-4}$ [Sander <i>et al.</i> , 2003]
Reaction probability for N <sub>2</sub> O <sub>5</sub> hydrolysis on sulfate aerosols	0.14 [Mozurkewich and Calvert, 1988]
Source of odd chlorine (by photolysis of chlorofluorocarbons, current conditions)	$15 \text{ cm}^{-3} \text{ s}^{-1}$
Source of odd nitrogen (by oxidation of nitrous oxide and transport from upper layers, current conditions)	$60 \text{ cm}^{-3} \text{ s}^{-1}$
Source of methane (by transport from the troposphere)	$10^4 \text{ cm}^{-3} \text{ s}^{-1}$
Dissipative loss frequency associated with transport	$0.8 \times 10^{-8} \text{ s}^{-1}$

oscillatory behavior in the ozone concentration with a period of tens of years.

[4] These earlier zero-dimensional model calculations were performed for a chemical scheme accounting for gas phase reactions only and therefore ignored the effects of chemical heterogeneous processes and of atmospheric transport. Heterogeneous reactions are important in the presence of polar stratospheric clouds and of aerosol particles, especially after large volcanic eruptions [Hofmann and Solomon, 1989; Granier and Brasseur, 1992]. In recent years both laboratory and modeling studies showed that heterogeneous reactions occurring on the surface of aerosols could lead to substantial ozone depletion [Worsnop *et al.*, 1988; Mozurkewich and Calvert, 1988; Tolbert *et al.*, 1988; Fried *et al.*, 1994; Hofmann and Solomon, 1989; Rodriguez *et al.*, 1991; Brasseur and Granier, 1992; World Meteorological Organization, 1992, 1998; Tie *et al.*, 1994; Bojkov, 1995]. During nonvolcanic periods a layer of background sulfate aerosols consisting of tiny liquid particles (mixture of water and sulfuric acid) is present in the stratosphere around 20–30 km altitude [Junge and Manson, 1961; Junge *et al.*, 1961]. The source of these sulfate aerosols is provided primarily by the photolysis of carbonyl sulfide, a relatively long-lived compound released by the oceans and the terrestrial biosphere and transported to the stratosphere, followed by chemical conversion to sulfate aerosols. During periods of low volcanic activity (background conditions) the surface area density ( $A$ ) provided by aerosols participating in heterogeneous reactions is of the order of  $0.5\text{--}1 \mu\text{m}^2 \text{ cm}^{-3}$ . However, after major volcanic eruptions, such as those of El Chichon in 1982 and Mount Pinatubo in 1991, large amounts of sulfur are injected into the stratosphere, and as a result, the stratospheric sulfate aerosol concentration is enhanced dramatically during the following 2–3 years. Observations show that after the Pinatubo eruption the aerosol surface area density reached about  $10\text{--}100 \mu\text{m}^2 \text{ cm}^{-3}$  [Hofmann and Solomon, 1989; Prather, 1992; McCormick and Veiga, 1992]. Higher values have probably occurred in the past after larger eruptions, and they should therefore be included in the range of all possible situations to be examined.

[5] The purpose of the present study is to analyze the behavior of the stratospheric photochemical system at

midlatitudes in the stratosphere near 25 km altitude and, specifically, to determine its response to large anthropogenic chlorine and nitrogen perturbations for different aerosol loads present in the stratosphere. This paper will therefore focus on the role of heterogeneous chemical reactions on the surface of sulfate aerosol particles at midlatitudes and will assess how these processes are susceptible to modification of the conclusions reached in the earlier study by Yang and Brasseur [2001]. In section 2 we briefly describe the model used in the present study. In section 3 we assess the response of the photochemical system to external forcing for different situations. In section 4 we discuss the results and present some conclusions.

## 2. Model

[6] The model used in the present study is a zero-dimensional model applied at 25 km altitude (midlatitudes) and is representative of the atmospheric layer in which ozone reached its maximum density. Details on the model conditions are given in Table 1. The chemical scheme adopted here (Tables 2a and 2b) is similar to the scheme used by Yang and Brasseur [2001] with, however, a few important modifications. Two heterogeneous reactions occurring on the surface of sulfate aerosols have been introduced:



Their role is to convert reactive nitrogen oxides into less reactive nitric acid and to activate chlorine by converting ClONO<sub>2</sub> into HOCl. This latter compound is easily photolyzed into Cl and OH. The rate constants adopted for these reactions are provided in Table 1. Other heterogeneous reactions that contribute to a lesser extent to chlorine activation and nitrogen conversion at midlatitudes have been ignored in this simple conceptual model.

[7] The gas phase reactions that lead to the formation and destruction of the Cl<sub>2</sub>O<sub>2</sub> dimer and contribute to

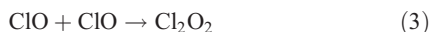
**Table 2a.** Chemical Reactions Used in the Model (at 220 K (25 km))

Reaction	Reaction Rate <sup>a,b</sup> , cm <sup>3</sup> s <sup>-1</sup>
O + O <sub>2</sub> + M → O <sub>3</sub> + M	1.0(-15)
O + O <sub>3</sub> → 2O <sub>2</sub>	6.86(-16)
O( <sup>1</sup> D) + N <sub>2</sub> → O + N <sub>2</sub>	2.97(-11)
O( <sup>1</sup> D) + O <sub>2</sub> → O + O <sub>2</sub>	4.40(-11)
H <sub>2</sub> O + O( <sup>1</sup> D) → 2OH	2.2(-10)
OH + O <sub>3</sub> → O <sub>2</sub> + HO <sub>2</sub>	2.23(-14)
HO <sub>2</sub> + O <sub>3</sub> → 2O <sub>2</sub> + OH	1.13(-15)
HO <sub>2</sub> + HO <sub>2</sub> → H <sub>2</sub> O <sub>2</sub> + O <sub>2</sub>	3.52(-12)
OH + H <sub>2</sub> O <sub>2</sub> → H <sub>2</sub> O + HO <sub>2</sub>	1.4(-12)
OH + HO <sub>2</sub> → H <sub>2</sub> O + O <sub>2</sub>	1.5(-10)
HO <sub>2</sub> + O → O <sub>2</sub> + OH	7.4(-11)
NO + O <sub>3</sub> → NO <sub>2</sub> + O <sub>2</sub>	3.45(-15)
NO <sub>2</sub> + O → NO + O <sub>2</sub>	1.12(-11)
NO <sub>2</sub> + O <sub>3</sub> → NO <sub>3</sub> + O <sub>2</sub>	1.75(-18)
NO <sub>2</sub> + NO <sub>3</sub> + M → N <sub>2</sub> O <sub>5</sub> + M	9.5(-13)
N <sub>2</sub> O <sub>5</sub> + M → NO <sub>2</sub> + NO <sub>3</sub> + M	6.83(-8)
NO <sub>2</sub> + OH + M → HNO <sub>3</sub> + M	4.16(-12)
HNO <sub>3</sub> + OH → NO <sub>3</sub> + H <sub>2</sub> O	2.88(-13)
NO + HO <sub>2</sub> → NO <sub>2</sub> + OH	1.09(-11)
Cl + O <sub>3</sub> → ClO + O <sub>2</sub>	8.9(-12)
ClO + O → Cl + O <sub>2</sub>	4.1(-11)
Cl + HO <sub>2</sub> → O <sub>2</sub> + HCl	3.9(-11)
Cl + CH <sub>4</sub> → HCl + CO + HO <sub>2</sub> + H <sub>2</sub> O	1.9(-14)
ClO + NO → Cl + NO <sub>2</sub>	2.4(-11)
ClO + NO <sub>2</sub> + M → ClONO <sub>2</sub> + M	4.2(-13)
ClO + HO <sub>2</sub> → HOCl + O <sub>2</sub>	1.2(-11)
HCl + OH → H <sub>2</sub> O + Cl	5.3(-13)
HOCl + OH → H <sub>2</sub> O + ClO	3.1(-13)
OH + CH <sub>4</sub> → 2H <sub>2</sub> O + CO + HO <sub>2</sub>	7.68(-16)
O( <sup>1</sup> D) + CH <sub>4</sub> → CO + 2H <sub>2</sub> O	1.4(-10)
CO + OH → HO <sub>2</sub> + CO <sub>2</sub>	1.5(-13)
ClO + ClO → Cl <sub>2</sub> O <sub>2</sub>	4.24(-14)

<sup>a</sup>Read, e.g., 1.0(-15) as  $1.0 \times 10^{-15}$ .

<sup>b</sup>For three-body reactions, equivalent second-order rate constants are calculated for air density of  $8.24(17) \text{ cm}^{-3}$  at 25 km.

substantial ozone depletion in regions of chlorine activation [Molina and Molina, 1987]



have also been added to the reaction scheme.

[8] Thus, in addition to the stable atmospheric constituents (O<sub>2</sub> and H<sub>2</sub>O), whose concentrations are fixed, the updated model includes 19 chemical species belonging to the oxygen, hydrogen, nitrogen, chlorine, and carbon families; 45 homogeneous chemical and photochemical reactions; and 2 heterogeneous reactions on the surface of sulfate aerosols. The effect of bromine (which is assumed to be small above 20 km altitude at midlatitudes) is neglected. Although kept relatively simple, the model captures the most important chemical processes that influence stratospheric ozone outside the polar regions. As in the model study of Yang and Brasseur [2001], the diurnal variation in the photodissociation coefficients of the chemical species is crudely represented: The photolysis frequencies in the sunlight atmosphere are expressed by their daytime average values, while the nighttime values are set equal to zero. The calculations are performed at 40°N for permanent equinox conditions. All concentrations reported

hereinafter are expressed as averages between the daytime and nighttime solutions. As with Yang and Brasseur [2001], the chemical system is solved using the Gear [1969] algorithm. Convergence of the solution to equilibrium is assumed to be reached when the first four digits of the concentration values for all species remain unchanged during at least 100 years of integration.

[9] The external sources and sinks for the photochemical system include the sources of odd nitrogen (NO<sub>y</sub> = NO + NO<sub>2</sub> + NO<sub>3</sub> + 2N<sub>2</sub>O<sub>5</sub> + HNO<sub>3</sub> + ClONO<sub>2</sub>) and odd chlorine (Cl<sub>y</sub> = Cl + ClO + ClONO<sub>2</sub> + 2Cl<sub>2</sub>O<sub>2</sub> + HOCl + HCl) resulting from the oxidation or photolysis of long-lived source gases produced at the surface and transported to the stratosphere: Odd nitrogen at 25 km arises from oxidation of nitrous oxide (N<sub>2</sub>O) and from downward transport of NO<sub>y</sub>. Odd chlorine is produced by photolysis of chlorofluorocarbons (CFCs). A source of methane S<sub>CH<sub>4</sub></sub> accounts for the injection of this compound from the troposphere. Its oxidation provides a source for carbon monoxide (CO), which is removed from the system by oxidation by OH (to form CO<sub>2</sub>) and by transport (L<sub>T</sub>). In this idealized model we assume that these source terms are external parameters, i.e., forcing terms that are not influenced by the solution of the system. In the real atmosphere, however, photolysis and oxidation processes of the source gases are sensitive to the chemical state of the atmosphere, but this feedback is ignored. To balance the system, the external sources must be balanced by loss processes. In the case of NO<sub>y</sub> and Cl<sub>y</sub>, it is assumed that these losses result from downward transport of air masses followed by wet scavenging of the soluble nitrogen and chlorine species in the troposphere. Since the simple conceptual model adopted here cannot treat the details of such complex processes, we make a simple assumption and add to all chemical equations a loss term assumed to be linear with the concentration of the corresponding compound. The associated loss frequency L<sub>T</sub> is chosen to be  $0.8 \times 10^{-8} \text{ s}^{-1}$  and corresponds to a time constant of approximately 4 years, i.e., close to the observed turnover time in the stratosphere. This simple formulation is used to assess the effect of linear dissipation on the system rather than to represent realistically the exchanges of chemical compounds between neighboring layers. A more rigorous formulation would require the use of a comprehensive chemical transport model, with explicit representation of advective and mixing processes that occur

**Table 2b.** Photolysis Reactions Used in the Model

Reaction	Photolysis Frequency, <sup>a,b</sup> s <sup>-1</sup>
O <sub>2</sub> + hν → O + O	2.5(-12)
O <sub>3</sub> + hν → O <sub>2</sub> + O( <sup>1</sup> D)	6.0(-05)
O <sub>3</sub> + hν → O <sub>2</sub> + O	5.4(-04)
H <sub>2</sub> O <sub>2</sub> + hν → 2OH	1.01(-05)
NO <sub>3</sub> + hν → NO <sub>2</sub> + O	1.56(-01)
NO <sub>3</sub> + hν → NO + O <sub>2</sub>	2.01(-02)
NO <sub>2</sub> + hν → NO + O	1.2(-02)
N <sub>2</sub> O <sub>5</sub> + hν → NO <sub>2</sub> + NO <sub>3</sub>	2.8(-05)
HNO <sub>3</sub> + hν → OH + NO <sub>2</sub>	1.9(-06)
ClONO <sub>2</sub> + hν → NO <sub>3</sub> + Cl	5.45(-05)
ClONO <sub>2</sub> + hν → NO <sub>2</sub> + ClO	6.05(-06)
HOCl + hν → OH + Cl	4.05(-04)
Cl <sub>2</sub> O <sub>2</sub> + hν → 2Cl + O <sub>2</sub>	2.30(-03)

<sup>a</sup>Read, e.g., 2.5(-11) as  $2.5 \times 10^{-12}$ .

<sup>b</sup>Daytime values on 15 March at 40°N.

**Table 3.** Modeling Results of Some Species for the Current State<sup>a</sup>

Case	O <sub>3</sub>	HO <sub>x</sub>	NO <sub>x</sub>	N <sub>2</sub> O <sub>5</sub>	HNO <sub>3</sub>	ClO <sub>x</sub>	HCl	ClONO <sub>2</sub>	CH <sub>4</sub>
Reference case <sup>b</sup>	0.447E + 13	0.911E + 07	0.117E + 10	0.189E + 09	0.507E + 10	0.785E + 08	0.867E + 09	0.856E + 09	0.101E + 13
No transport <sup>c</sup>	0.481E + 13	0.990E + 07	0.931E + 09	0.163E + 09	0.420E + 10	0.878E + 08	0.667E + 09	0.815E + 09	0.965E + 12
Yang and Brasseur [2001] <sup>d</sup>	0.489E + 13	0.735E + 07	0.198E + 10	0.572E + 09	0.420E + 10	0.374E + 08	0.667E + 09	0.639E + 09	0.102E + 13

<sup>a</sup>Number density is given in cm<sup>-3</sup>. Read, for example, 0.447E + 13 as 0.447 × 10<sup>13</sup>.

<sup>b</sup>For the reference case (see Tables 1, 2a, and 2b),  $A = 1 \mu\text{m}^2 \text{cm}^{-3}$ ,  $S_{\text{Cl}} = 15 \text{cm}^{-3} \text{s}^{-1}$ ,  $S_{\text{N}} = 60 \text{cm}^{-3} \text{s}^{-1}$ , and  $L_T = 0.8 \times 10^{-8} \text{s}^{-1}$ .

<sup>c</sup>Dissipation associated with transport is ignored, but heterogeneous processes are taken into account (reactions (1) and (2); see text), with  $A = 1 \mu\text{m}^2 \text{cm}^{-3}$ . Details on the model assumptions are given in the text.

<sup>d</sup>Dissipation by transport and heterogeneous processes are neglected.

at different temporal and spatial scales. Under the simple assumptions adopted here, the concentrations of odd chlorine Cl<sub>y</sub> and odd nitrogen NO<sub>y</sub> are fully determined by the balances between their source and transport terms, which, in the model, do not change as a function of time. Photochemistry affects only the partitioning of species within the chemical families and the concentration of the other compounds such as ozone and OH. The asymptotic solutions for the concentration of odd chlorine and odd nitrogen are  $[\text{Cl}_y] = S_{\text{Cl}}/L_T$  and  $[\text{NO}_y] = S_{\text{N}}/L_T$ , respectively. The mixing ratios of NO<sub>y</sub> and Cl<sub>y</sub> (expressed in ppbv) at 25 km altitude are therefore obtained by multiplying by 0.15 the source terms  $S_{\text{N}}$  and  $S_{\text{Cl}}$  (expressed in cm<sup>-3</sup> s<sup>-1</sup>). For present conditions the mixing ratios of NO<sub>y</sub> and Cl<sub>y</sub> at 25 km are equal to 9 and 2.25 ppbv, respectively. By eliminating  $L_T$  we note, in addition, that  $[\text{Cl}_y]/[\text{NO}_y] = S_{\text{Cl}}/S_{\text{N}}$ ; that is, the concentration ratio between odd chlorine and odd nitrogen is constrained by the ratio between the external sources  $S_{\text{Cl}}$  and  $S_{\text{N}}$ .

[10] Table 3 shows the current state of the system derived for an aerosol surface area density  $A$  of  $1 \mu\text{m}^2 \text{cm}^{-3}$ . From Table 3 it can be seen that the ozone concentration of  $4.47 \times 10^{12} \text{cm}^{-3}$  calculated by the model is representative of the values observed near 25 km altitude [see, e.g., Brasseur and Solomon, 1986; U.S. Standard Atmosphere, 1976].

[11] For comparison with the pure gas phase model considered by Yang and Brasseur [2001], we will also assess the behavior of the photochemical system in a case that accounts for heterogeneous reactions on sulfate aerosol particles (reactions (1)–(4)) but, as in the previous study, ignores the dissipative effects associated with transport. To be consistent with the assumptions made by Yang and Brasseur [2001], in this particular model case the NO<sub>y</sub> and Cl<sub>y</sub> sources ( $S_{\text{N}} = 42 \text{cm}^{-3} \text{s}^{-1}$  and  $S_{\text{Cl}} = 20 \text{cm}^{-3} \text{s}^{-1}$ ) applied to the system will be balanced by some linear loss terms for HNO<sub>3</sub> ( $10^{-8} \text{s}^{-1}$ ) and HCl ( $3 \times 10^{-8} \text{s}^{-1}$ ), which leads to a calculated state of the atmosphere that is very close to the observed conditions at 25 km altitude (see Table 3). In section 3 this model will be used to assess the nonlinear response of stratospheric ozone and other chemical species to increasing values of the aerosol surface area density  $A$  and of the stratospheric source (or abundance at 25 km) of odd chlorine and nitrogen.

### 3. Response of the Photochemical System

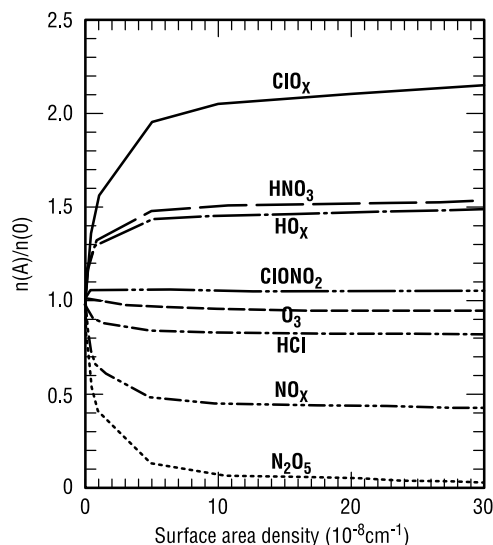
#### 3.1. Dependence of the Solution on the Aerosol Surface Area

[12] We first consider the case in which NO<sub>y</sub> and Cl<sub>y</sub> sources ( $60$  and  $15 \text{cm}^{-3} \text{s}^{-1}$ , respectively) correspond to

the background situation and the mixing ratios of odd nitrogen and odd chlorine are equal to 9 and 2.25 ppbv, respectively. Figure 1 shows the changes in the concentration of various chemically active compounds when the aerosol surface area density  $A$  increases from zero (pure gas phase case) to  $30 \mu\text{m}^2 \text{cm}^{-3}$  (large volcanic perturbation). As expected, we note a reduction in the NO<sub>x</sub> concentration (factor of 2 for  $A$  increasing from 0 to  $10 \mu\text{m}^2 \text{cm}^{-3}$ ) and an increase in the HNO<sub>3</sub> abundance (factor of 1.5 for  $A$  changing from 0 to  $10 \mu\text{m}^2 \text{cm}^{-3}$ ) due to enhanced heterogeneous conversion on the surface of aerosol particles. Chlorine activation is also predicted, with a factor of 2 enhancement in the ClO<sub>x</sub> ( $\text{ClO}_x = \text{Cl} + \text{ClO} + 2 \text{Cl}_2\text{O}_2$ ) mixing ratio for  $A$  increasing from 0 to  $10 \mu\text{m}^2 \text{cm}^{-3}$ . No abrupt change is predicted by the model, and the reduction in the ozone concentration never exceeds 7% at the model level of 25 km. The saturation process, highlighted by Fahey *et al.* [1993], is visible; the dependence of the solution with the aerosol load becomes very small as the value of  $A$  increases beyond, typically,  $5\text{--}10 \mu\text{m}^2 \text{cm}^{-3}$ .

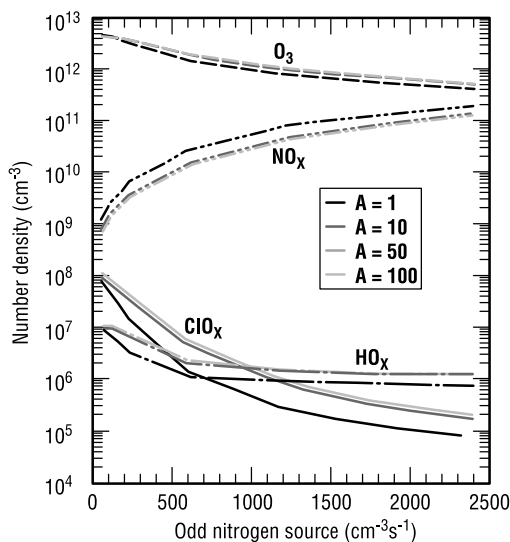
#### 3.2. Response to Changes in the Source ( $S_{\text{N}}$ ) of Odd Nitrogen

[13] Figure 2 shows the dependence of the solution with increasing values of the odd nitrogen sources  $S_{\text{N}}$  (and



**Figure 1.** Dependence of the states of the photochemical system on the aerosol surface area density  $A$ , where  $A = 0$  represents the pure gas phase conditions. Dissipation associated with atmospheric transport is included.





**Figure 2.** Dependence of the states of the photochemical system on the odd nitrogen source  $S_N$  for different values of the aerosol surface area density  $A$  as the chlorine source strength  $S_{Cl} = 15 \text{ cm}^{-3} \text{ s}^{-1}$  (current value). Dissipation associated with atmospheric transport is included.

mixing ratio) for different values of the aerosol surface area density  $A$  and for  $S_{Cl} = 15 \text{ cm}^{-3} \text{ s}^{-1}$  ( $Cl_y$  mixing ratio of 2.25 ppbv). As  $S_N$  increases from its current value of  $60 \text{ cm}^{-3} \text{ s}^{-1}$  to  $2500 \text{ cm}^{-3} \text{ s}^{-1}$ , the abundance of  $NO_x$  increases by more than 2 orders of magnitude, while that of  $ClO_x$  decreases by a factor of 1000. The abundance of  $HO_x$  is reduced by a factor of 10. The response varies somewhat with the value of the surface area density. The response of the system is clearly nonlinear, but even with unrealistically large  $NO_y$  perturbations, abrupt transitions such as those found in the model of *Yang and Brasseur* [2001] (in which heterogeneous chemistry was ignored) cannot be found.

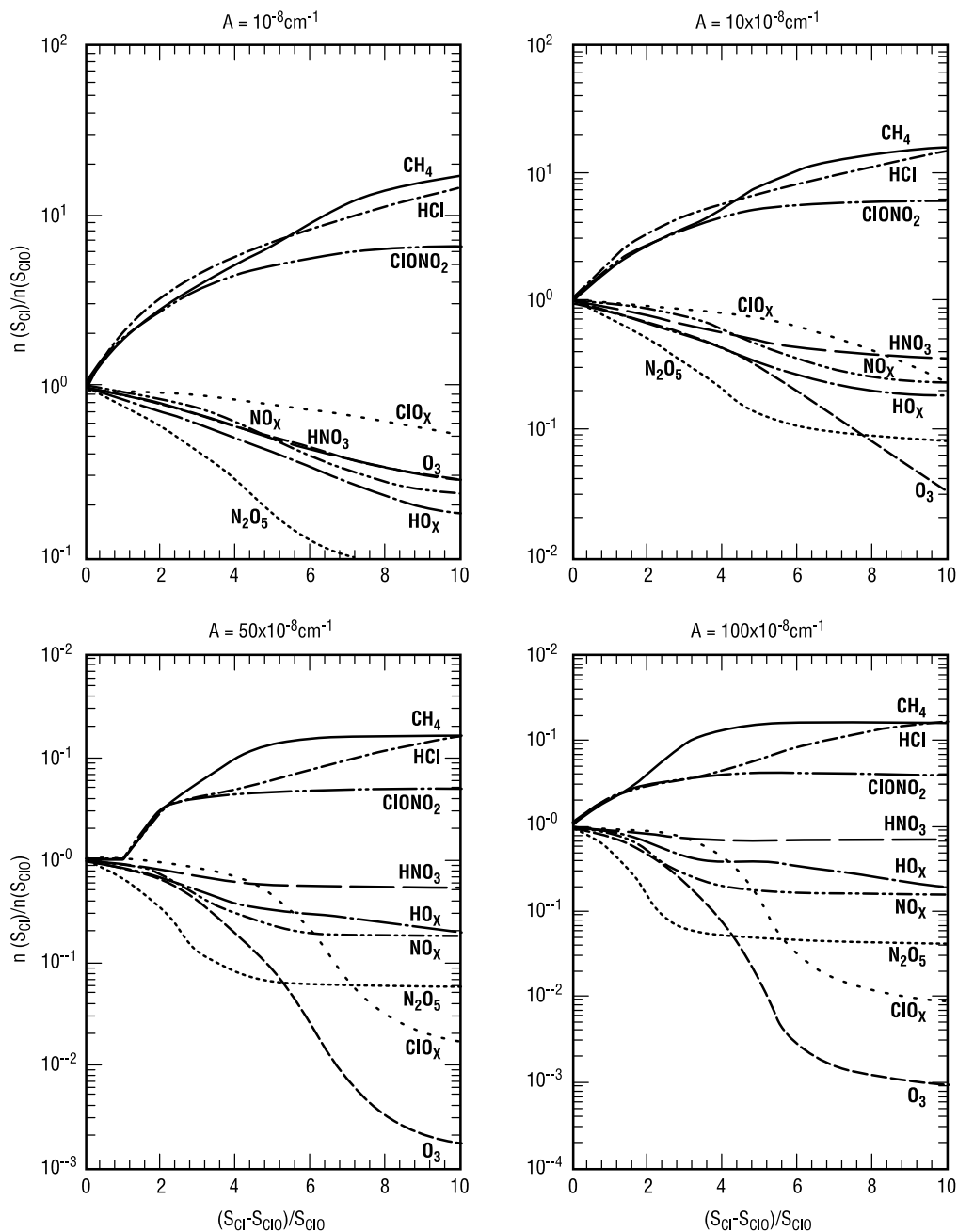
### 3.3. Response to Changes in the Source ( $S_{Cl}$ ) of Odd Chlorine

[14] Figure 3 shows the response of the system when the source  $S_{Cl}$  and mixing ratio of odd chlorine increase by a factor of 10. The model results are displayed for different values of the aerosol surface area density (from 1 to  $100 \mu\text{m}^2 \text{ cm}^{-3}$ ) and for the background level of  $NO_y = 9 \text{ ppbv}$  (or  $S_N = 60 \text{ cm}^{-3} \text{ s}^{-1}$ ). Again, even though no catastrophic transition is noticeable, the state of the system responds in a highly nonlinear way [*Cicerone et al.*, 1983; *Prather et al.*, 1984] to the value of parameter  $S_{Cl}$ , in particular for high values of the aerosol surface area density  $A$ . For an increase of a factor of 10 in  $S_{Cl}$  (corresponding to a change in the  $Cl_y$  mixing ratio from 2.3 to 22.5 ppbv) the ozone concentration decreases by factors of 4, 30, 500, and 1000 when  $A$  is equal to 1, 10, 50, and  $100 \mu\text{m}^2 \text{ cm}^{-3}$ , respectively. Figure 3 also shows that for aerosol parameters  $A$  larger than 50 the concentration of most species approaches a saturation value when the abundance of  $Cl_y$  exceeds about 4 times its background value, except in the case of  $O_3$ ,  $Cl$ ,  $CH_4$ , and  $HCl$ . Under these conditions the ozone destruction is determined primarily by the concentration of chlorine.

[15] The sensitivity of the ozone density to the odd chlorine source  $S_{Cl}$  is represented in Figure 4 for different values of the aerosol surface area density  $A$ . This diagram shows that the value of  $S_{Cl}$  for which the ozone/chlorine sensitivity  $\gamma = 1/[O_3] \times d[O_3]/dS_{Cl}$  reaches a maximum decreases with the aerosol surface area density  $A$ , and at the same time the amplitude  $\gamma_{max}$  of this maximum sensitivity increases with  $A$ . Thus, as parameter  $A$  increases, the stability of the system decreases, and for aerosol loads even higher than those considered here, a multiequilibrium regime could possibly be found.

### 3.4. Role of Dissipation

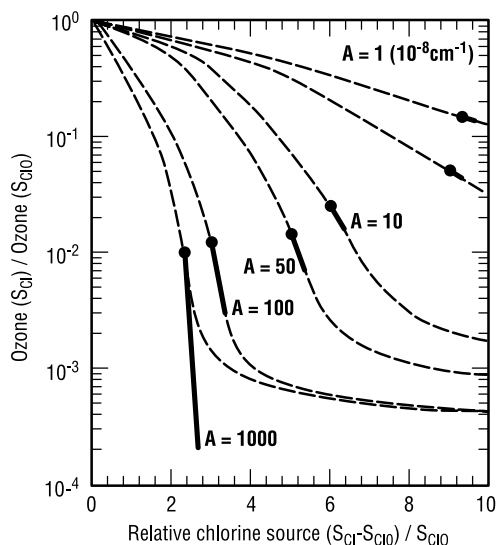
[16] In order to assess the effect of dissipative transport processes on the response of the system, we have considered several cases with different values of the linear dissipative term ( $L_T$ ). As indicated in section 2, the formulation adopted here is simple and does not represent realistically the complex and scale-dependent processes that determine atmospheric transport. The first case corresponds to a value of  $L_T = 0$  (no dissipation associated with transport). The response of the system to increasing values of the surface area density (from 1 to  $500 \mu\text{m}^2 \text{ cm}^{-3}$ ) calculated under these assumptions for current levels of  $NO_y$  and  $Cl_y$  is shown in Figure 5. It is very different from the cases discussed in sections 3.1, 3.2, and 3.3, in which a linear transport term was applied to the equations of all species. In this case without dissipation associated with transport, two stable equilibrium solution branches in the state-parameter space are found, with the first equilibrium branch defined for the aerosol surface area density  $A \leq 429 \mu\text{m}^2 \text{ cm}^{-3}$  and the second branch present for  $A \geq 163 \mu\text{m}^2 \text{ cm}^{-3}$ . Obviously, the interval [163, 429] is characterized by a multiequilibrium solution. In fact, there should also be at least one unstable equilibrium solution in this interval [*Joseph*, 1976], even though it is not explicitly resolved by the model. Near each end point of this interval a critical transition occurs. The point corresponding to  $A = 429 \mu\text{m}^2 \text{ cm}^{-3}$  is referred to as the "attack catastrophic point," while the point at which  $A = 163 \mu\text{m}^2 \text{ cm}^{-3}$  is called the "retreat catastrophic point" [*Zeeman*, 1976]. If parameter  $A$  increases and exceeds the attack point, a catastrophic transition occurs from the first equilibrium branch to the second one. This transition corresponds to abrupt changes in the concentrations of most chemical compounds. Specifically, at this point the ozone density is reduced by about 3 orders of magnitude. The concentration of  $NO_x$  is reduced by almost a factor of 2.5, while that of  $ClO_x$  is enhanced by the same factor. The concentration of  $HO_x$  is reduced by a factor of 1.3. The partitioning between chemical family members is also strongly modified: The ratio between the  $HO_2$  and  $OH$  concentrations is reduced from a value of typically 4 (first branch) to  $10^{-2}$  (second branch). Within the  $ClO_x$  family the  $Cl/ClO$  concentration ratio changes from  $1.0 \times 10^{-4}$  to  $5.0 \times 10^{-2}$  during the abrupt transition. The large increase in the  $Cl$  concentration (factor of 2000) explains the dramatic reduction in the methane concentration. On the second branch of the solution, ozone is controlled primarily by the chlorine species, with almost no direct influence from nitrogen species. If parameter  $A$  decreases and encounters the retreat point, another catastrophic transition happens, and the system returns abruptly



**Figure 3.** Dependence of the states of the photochemical system on the odd chlorine source  $S_{Cl}$  for different values of the aerosol surface area density  $A$  as the nitrogen source strength  $S_N = 60 \text{ cm}^{-3} \text{ s}^{-1}$  (current value). Dissipation associated with atmospheric transport is included.

to the first equilibrium branch. Obviously, this is a standard “fold” catastrophe with delay [Zeeman, 1976]. On the first equilibrium branch, closest to the current state of the system, the sensitivity of the system to changes in parameter  $A$  is relatively small. For example, when  $A$  varies from 10 to  $100 \mu\text{m}^2 \text{ cm}^{-3}$  (typical values of aerosol levels following large volcanic eruptions like those of Pinatubo), the ozone concentration decreases by 6% only, highlighting the saturation of the system relative to the conversion of  $\text{NO}_x$  to  $\text{HNO}_3$  [Fahey et al., 1993]. The dependence of the ozone concentration on changes in the aerosol surface area remains therefore relatively limited as long as the value of  $A$  remains below a threshold value.

[17] Figure 6 shows the solutions of the system to increasing sources of odd chlorine for  $20 \leq S_{Cl} \leq 150 \text{ cm}^{-3} \text{ s}^{-1}$  and for the value of  $A$  fixed at 1, 10, 100, and  $150 \mu\text{m}^2 \text{ cm}^{-3}$ . For a background aerosol load with  $A = 1$  (see Figure 6a), no multiequilibrium structure is found, but a sharp concentration gradient is visible over interval  $100 \leq S_{Cl} \leq 120 \text{ cm}^{-3} \text{ s}^{-1}$ . As the value of  $A$  increases, the width of this interval decreases, and the concentration gradient increases. When reaching a value of  $A = 6 \mu\text{m}^2 \text{ cm}^{-3}$ , the concentration curves break into two separate branches (multiequilibrium regime) near  $S_{Cl} = 78 \text{ cm}^{-3} \text{ s}^{-1}$ . When  $A = 10 \mu\text{m}^2 \text{ cm}^{-3}$  (see Figure 6b), the first equilibrium branch of the system is defined for  $S_{Cl}$  located on interval



**Figure 4.** Dependence of the ozone concentration on parameter  $S_{Cl}$  for different values of the aerosol load (expressed in  $\mu\text{m}^2 \text{cm}^{-3}$  or  $10^{-8} \text{cm}^{-1}$ ). The solid dots show the points with the maximum slope (or maximum ozone chlorine sensitivity), and the solid lines show the absolute values of the corresponding slopes.

[20, 71], which corresponds to the current state branch. The second branch is present over interval [67, 150], so that multiequilibrium solutions correspond to interval [67, 71]. When  $S_{Cl}$  increases from its current value (denoted by dots) and reaches the attack catastrophic point near  $S_{Cl} = 71 \text{ cm}^{-3} \text{ s}^{-1}$ , which corresponds to a 2.5-fold increase in  $S_{Cl}$ , the state of the system jumps from the first branch to the second one with an abrupt reduction (of nearly a factor of 50) in the ozone concentration. Dramatic changes in the concentration of other chemical compounds (enhanced  $\text{ClO}_x$  and reduced  $\text{NO}_x$  and  $\text{HO}_x$  densities) are also predicted. As the aerosol surface area density increases, the width of the parameter interval corresponding to multiequilibrium solutions increases, and the location of this interval gets closer to the current value of  $S_{Cl}$ .

[18] It should be noted that although the dissipative effects associated with transport are ignored in both cases, the behavior of the system versus  $\text{Cl}_y$ , discussed here is very different from the case described by Yang and Brasseur [2001], in which only gas phase chemistry is considered. When heterogeneous reactions are added to the system, only equilibrium solutions are obtained. The periodic oscillations and the birhythmicity phenomena found in the early study disappear and are replaced by a multiequilibrium regime.

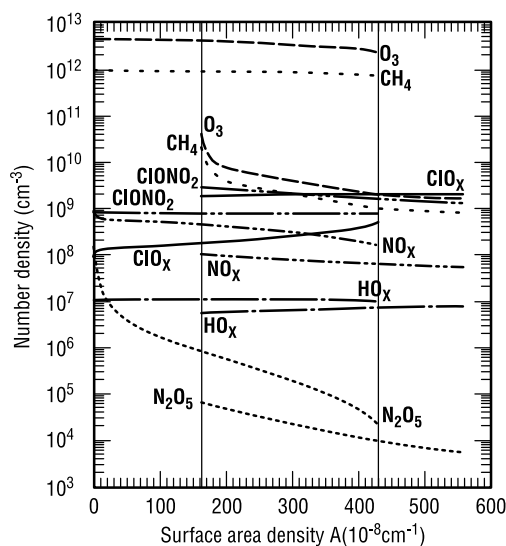
[19] The response of the photochemical system (ignoring dissipation resulting from transport) was also investigated as a function of the odd nitrogen source  $S_N$  and aerosol surface area density  $A$  (see Figure 7). In this analysis the value of parameter  $S_{Cl}$  was kept at its current value, and parameter  $S_N$  took values in the interval ranging from 1 to  $2100 \text{ cm}^{-3} \text{ s}^{-1}$ . As in the case for  $\text{Cl}_y$  perturbations the photochemical system is characterized by multiequilibrium regimes. Again, the interval width corresponding to multiequilibrium solutions increases with the value of the aerosol surface area density  $A$ . However, contrary to what is observed in the case

shown in Figure 6, the multiequilibrium regime does not vanish for the smallest values of  $A$ , including  $A = 0$  (which corresponds to the gas phase case).

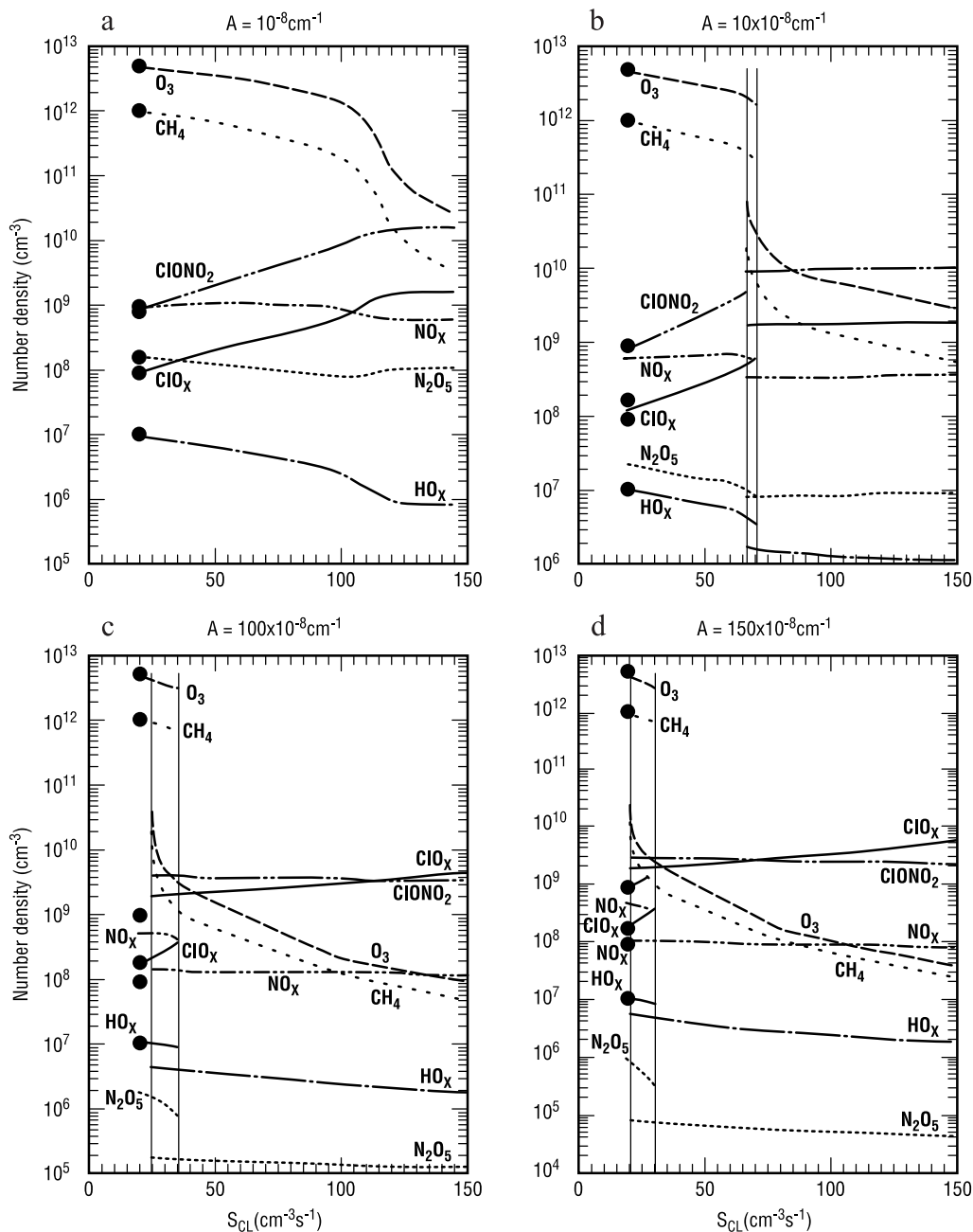
[20] The introduction of linear dissipation (transport) terms in the model equations leads to the disappearance of the multiequilibrium regime and of the catastrophic transition in the solution of the photochemical system. More specifically, as coefficient  $L_T$  increases, starting from zero, the multiequilibrium regime gradually disappears. For small values of  $L_T$  (e.g.,  $0.01 \times 10^{-8} \text{ s}^{-1}$ ), no obvious changes happen compared with the solution structure shown in Figure 6, except for a small drift in the critical values associated with the catastrophic transitions and a small change in the width of the parameter interval corresponding to the multiequilibrium solutions. As  $L_T$  further increases (reaching, e.g.,  $0.1 \times 10^{-8} \text{ s}^{-1}$ ), the multiequilibrium structure disappears for the aerosol parameter  $A = 10 \mu\text{m}^2 \text{cm}^{-3}$  but still exists for  $A = 100 \mu\text{m}^2 \text{cm}^{-3}$ . This shows that a transition happens when  $L_T$  passes through a certain threshold value located between  $0.01 \times 10^{-8}$  and  $0.1 \times 10^{-8} \text{ s}^{-1}$ . For  $L_T = 0.2 \times 10^{-8} \text{ s}^{-1}$  the multiequilibrium regime with the catastrophic transitions vanishes for all values of  $A$  under consideration and is replaced by a continuous structure similar to that shown in Figure 3. Thus the system undergoes a bifurcation when  $L_T$  increases from  $0.1 \times 10^{-8}$  to  $0.2 \times 10^{-8} \text{ s}^{-1}$ , and the sharp concentration gradient structure observed for larger values of the aerosol load should thus be regarded as a degeneracy of the multiequilibrium regime.

#### 4. Discussion and Conclusions

[21] Stratospheric sulfate aerosols affect the concentrations of  $\text{ClO}_x$  and  $\text{NO}_x$  through heterogeneous reactions and, as a result, influence the concentration of ozone. The mechanisms involved are the following: First, heterogeneous reactions (e.g., reaction (1)) convert chlorine reservoirs ( $\text{ClONO}_2$  and  $\text{HCl}$ ) into more reactive compounds



**Figure 5.** Dependence of the states of the photochemical system on the aerosol surface area density when dissipation associated with transport is ignored.



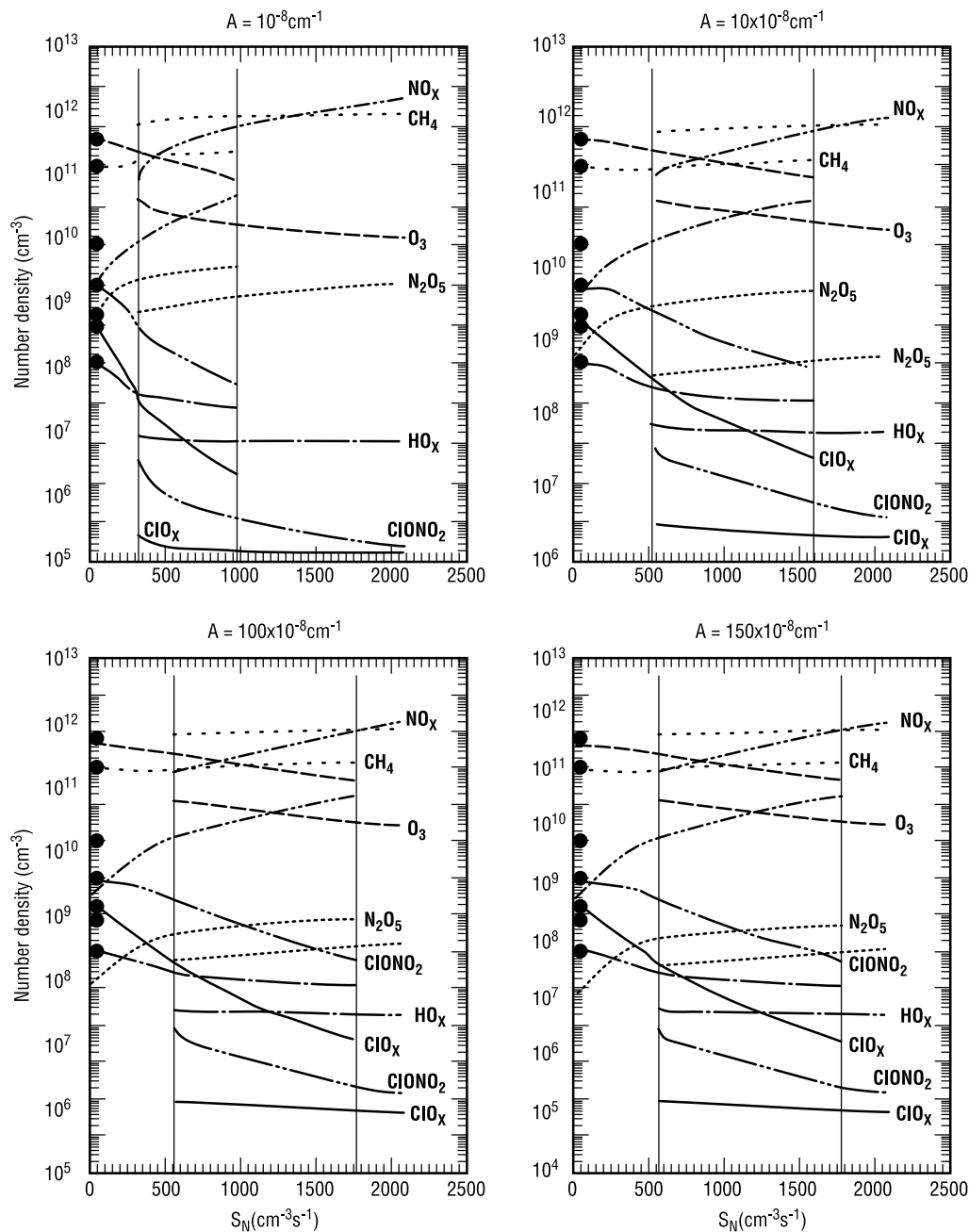
**Figure 6.** Dependence of the states of the photochemical system on the aerosol surface area density  $A$  and on the odd chlorine source  $S_{Cl}$  when dissipation associated with transport is ignored: (a)  $A = 710^{-8} \text{ cm}^{-1}$ , (b)  $A = 10 \times 10^{-8} \text{ cm}^{-1}$ , (c)  $A = 100 \times 10^{-8} \text{ cm}^{-1}$ , (d)  $A = 150 \times 10^{-8} \text{ cm}^{-1}$ .

(HOCl and  $\text{Cl}_2$ ), which leads to enhanced concentrations of ClO as a result of their photolysis by solar radiation. At the same time, heterogeneous reactions (e.g., reactions (1) and (2)) convert reactive nitrogen oxides into nitric acid ( $\text{HNO}_3$ ). The decrease in the  $\text{NO}_2$  density tends to reduce the conversion rate of ClO into  $\text{ClONO}_2$  and of OH into  $\text{HNO}_3$ . At the same time, because of enhanced abundances of stratospheric OH, the concentrations of Cl and hence of ClO are increased as a result of faster conversion of HCl to reactive chlorine. Thus the net effect of the heterogeneous chemistry is to enhance the stratospheric levels of reactive chlorine and of hydroxyl radicals and, at the same time, to

reduce the level of reactive nitrogen. Under these conditions, stratospheric ozone appears to be increasingly controlled by chlorine rather than by nitrogen species. This situation becomes more pronounced as the aerosol surface area density  $A$  increases, and hence the rate of chlorine activation is enhanced.

[22] The behavior of the system should be examined in the three-dimensional (3-D) parameter space  $P(S_N, S_{Cl}, A)$ . However, in order to reduce the number of computer resources needed, while focusing on the most interesting problems, a proper domain in the parameter space was selected. The photochemical behavior of the system has





**Figure 7.** Dependence of the states of the photochemical system on the aerosol surface area density  $A$  and on the odd nitrogen source  $S_N$  when dissipation associated with transport is ignored.

therefore been examined for specific conditions in specific 2-D subspaces where one of the external parameters such as  $S_{Cl}$  (or  $S_N$ ) remains constant.

[23] In the pure photochemical case where transport is neglected, the solutions of the photochemical system expressed as a function of aerosol parameter  $A$  (when parameters  $S_N$  and  $S_{Cl}$  take their current values) are characterized by a multiequilibrium regime and a fold catastrophe manifold. Multiequilibrium regimes are also predicted when considering the dependence of the solutions on parameters  $S_N$  and  $S_{Cl}$  for different levels of the aerosol load. It is not difficult to infer that in these cases the structure of the solutions is characterized by two cusp catastrophe manifolds.

[24] When a linear dissipation term is added to the photochemical equations to account for the effects of transport, the multiequilibrium regime observed in the pure photochemical case disappears (compare Figures 2 and 3 to Figures 7 and 6, respectively). Dissipation tends to stabilize the system and hence to avoid catastrophic transitions in the concentration of ozone and other chemical species. The lack of abrupt changes does not imply that the ozone density becomes insensitive to external sources. For example, as shown by Figures 3 and 4, the ozone concentration drops almost exponentially with the chlorine source for certain values of the chlorine source  $S_{Cl}$  and of the aerosol surface area  $A$ . The behavior of stratospheric ozone is better understood when it is realized that its

nonlinear response to external forcing is characterized by a degeneracy of a multiequilibrium regime.

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