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STRATOSPHERIC CHEMISTRY: MULTIPLE SOLUTIONS

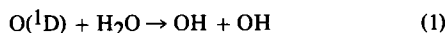M. J. Prather, M. B. McElroy, S. C. Wofsy, J. A. Logan

Center for Earth and Planetary Physics, Harvard University, Cambridge, Mass.

Abstract. It is shown that the equations describing chemical partitioning among Cl_x (HCl, Cl, ClO, $ClNO_3$), NO_t (NO, NO_2, NO_3, N_2O_5, HNO_2, $ClNO_3$) and HO_x (OH, HO_2) may admit multiple solutions. These solutions apply to the high latitude winter stratosphere where abrupt spatial variations may be expected for NO_2, ClO and $ClNO_3$.
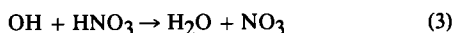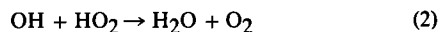
Present models for stratospheric chemistry involve more than twenty species which interact through a complex set of chemical reactions. Concentrations of individual compounds are obtained by solving an appropriate set of kinetic equations. These equations are intrinsically non-linear and it is apparent that they may admit the possibility of multiple solutions.

It is usually assumed that only one solution has physical significance, that alternate roots should involve negative or imaginary values for species concentrations. It appears, however, that this assumption is unjustified and that multiple solutions may indeed occur under conditions arising in lower regions of the winter stratosphere. The existence of widely disparate solutions to the kinetic equations could provide an explanation for some puzzling features in the observed distribution of stratospheric NO_2.

The chemistry of the lower stratosphere is regulated by HO_x (OH, HO_2), Cl_x (HCl, Cl, ClO, $ClNO_3$) and NO_x (NO, NO_2, NO_3, N_2O_5, HNO_2, $ClNO_3$, HNO_3). In most of the illuminated stratosphere HO_x is formed by

$$O(^1D) + H_2O \rightarrow OH + OH \tag{1}$$

and removed by

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{2}$$

$$OH + HNO_3 \rightarrow H_2O + NO_3 \tag{3}$$
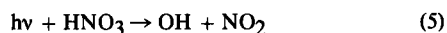
and

$$OH + NO_2 + M \rightarrow HNO_3 + M \tag{4}$$

Reaction (4) dominates OH removal at high latitudes in winter. Under these conditions the concentration of $O(^1D)$ is very small and the major source of HO_x is
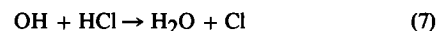
$$hv + HNO_3 \rightarrow OH + NO_2 \tag{5}$$

rather than reaction (1).

The lifetime of HNO_3 is exceedingly long in the winter stratosphere and HNO_3 behaves as a passive tracer whose spatial distribution is determined mainly by transport. Time constants are short for chemical interchange among other members of the NO_x family. Relative concentrations for members of this subset, NO_t (NO, NO_2, NO_3, N_2O_5, HNO_2, $ClNO_3$), are determined by a balance of local chemical reactions. Mixing ratios for HNO_3 and NO_t are shown for two representative latitudes in Figure 1.

Interchange between members of the Cl_x family involves a sequence of reversible transformations,

$$HCl \longleftrightarrow Cl \longleftrightarrow ClO \longleftrightarrow ClNO_3, \tag{6}$$
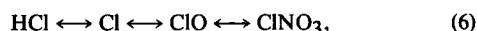
regulated in large measure by OH, NO and NO_2, through the reactions

$$OH + HCl \rightarrow H_2O + Cl \tag{7}$$

$$ClO + NO \rightarrow Cl + NO_2 \tag{8}$$

and

$$ClO + NO_2 + M \rightarrow ClNO_3 + M. \tag{9}$$

The concentration of Cl_x exceeds that of NO_t in the lower stratosphere, as is evident in Figure 1. The manner in which the concentration of ClO varies as a function of Cl_x is shown in Figure 2 for several altitudes at 60°N, winter.

The general behavior exhibited by the various curves in Figure 2 may be readily understood. The concentration of ClO varies linearly as a function of Cl_x at low concentrations of Cl_x, with approximately 0.1% of Cl_x present as ClO. The concentration of ClO varies linearly with Cl_x also at high concentrations of Cl_x where ClO is the dominant component. The transition from the low to the high Cl_x regimes exhibits behavior analogous to that observed in the titration of a weak acid with a strong base. Addition of Cl_x in the presence of limited quantities of NO_t ensures almost complete conversion of NO_t to $ClNO_3$. The concentration of NO_2 under these conditions is set by a balance of (9) and

$$hv + ClNO_3 \rightarrow ClO + NO_2. \tag{10}$$
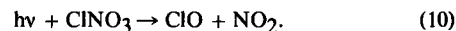
Thus the concentration of NO_2 varies inversely with that of ClO.

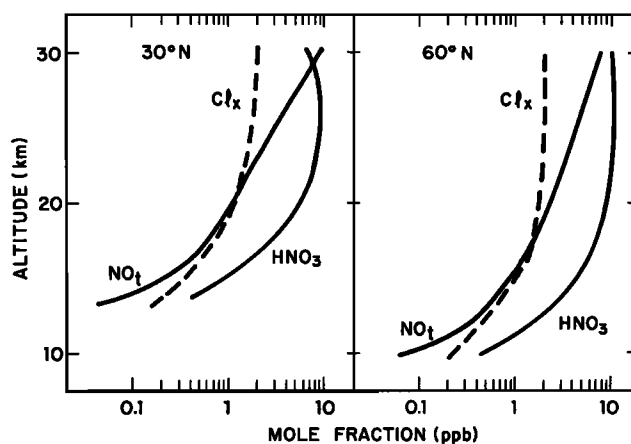The relative abundances of NO and NO_2 at low concentrations of ClO are set by

Fig. 1. Stratospheric profiles of Cl_x, NO_t and HNO_3 for 30°N and 60°N latitude in winter. the 30°N profile is based on the one-dimensional calculations of Logan et al. (1978) in which NO_t and HNO_3 are allowed to diffuse separately. The 60°N values assume transport along mixing surfaces with allowances for NO_t-HNO_3 photochemical equilibration over a period of two months. The chemical scheme is from Logan et al. (1978) with updated rates for the reactions $HO_2 + NO$ (3.3 x 10^{-12} exp[+225/T]) and $HO_2 + O_3$ (1.4 x 10^{-14} exp[-580/T]) from Howard and Zahniser (private communication).
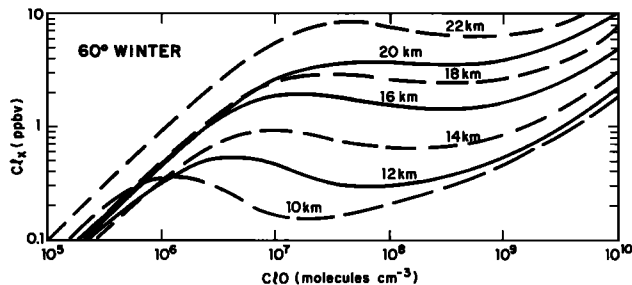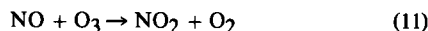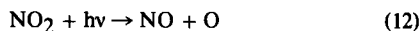
Fig.2. Total Cl_x as a function of ClO number density for several altitudes in the lower stratosphere at 60°N in winter. The NO_t and HNO_3 profiles are taken from Figure 1. The calculations use 24-hour-average insolation and assume achievement of a photochemical steady state.

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{11}$$

and

$$NO_2 + h\nu \rightarrow NO + O \tag{12}$$

In this case the concentration of NO is proportional to that of NO_2. At high concentrations of ClO, (8) may be more important than (11) and the concentration of NO may change from an inverse to an inverse-square dependence on ClO. The rate at which ClO is recycled (reaction 8) tends to a constant, independent of ClO, and ultimately decreases with further increase in the concentration of ClO. The concentration of ClO in the transition zone may increase rapidly with small additions of Cl_x until ClO represents the dominant form of Cl_x.

The variation of HCl, Cl, OH, NO, NO_2 and $ClNO_3$ as a function of ClO at 16 km is illustrated in Figure 3. The maximum observed for HCl is of particular interest, in that the occurrence of this feature allows the possibility of multiple solutions for ClO over an interesting range of values for Cl_x. The presence of a maximum reflects the manner in which OH depends on NO_2 and, therefore, on ClO. The concentration of HCl varies as the ratio [Cl]/[OH]. As may be seen from the figure, Cl is relatively constant near the HCl maximum, while OH increases rapidly with increasing ClO in response to the associated drop in NO_2.

Figure 4 shows the range of concentrations for ClO and NO_2 calculated for a solar declination of -20° along a mixing surface
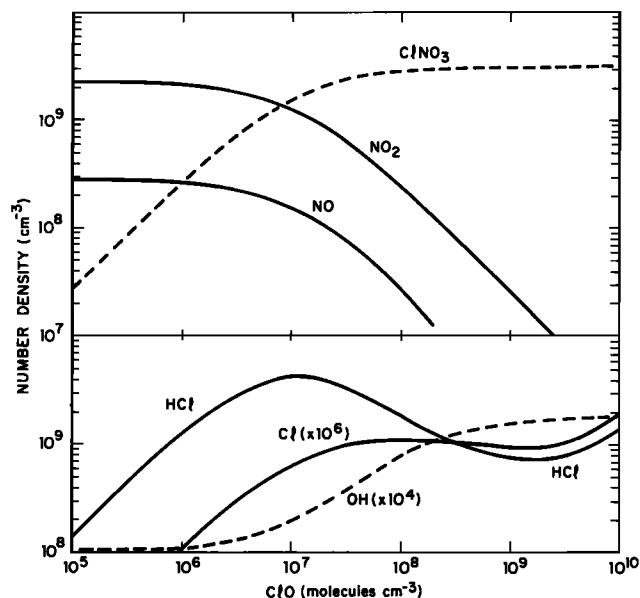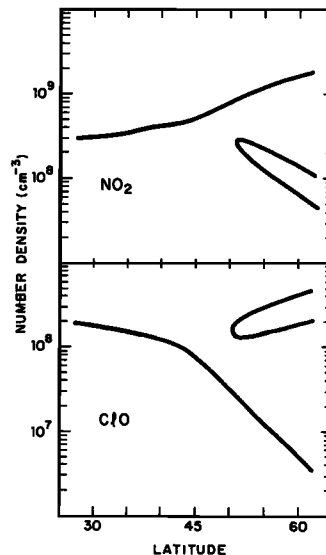

Fig.4. Mean values for the concentration of ClO and NO_2 along a mixing surface extending from 30°N (20 km) to 60°N (16 km) under winter conditions. Note appearance of a second set of solutions above 50°. Calculations use mole fractions of Cl_x, NO_t, and HNO_3 equal to 1.4, 1.0 and 5.5 ppb, respectively.

extending from 30°N, 20 km to 60°N, 16 km. Results shown here were derived using procedures described by Logan et al. (1978), with volume mixing ratios for NO_t, HNO_3 and Cl_x set equal to 1.0×10^{-9}, 5.5×10^{-9}, and 1.4×10^{-9} respectively. The computations are intended to illustrate the point that quite different solutions may arise under fixed external conditions at a given location. The particular example shown in Figure 4 is not unique. Similar behavior may be obtained for a range of altitudes in the lower stratosphere for which the concentration of Cl_x exceeds NO_t, a necessary but not sufficient condition.

It is obviously difficult to provide a detailed account for the chemical history of air parcels in lower regions of the winter stratosphere. Our study indicates that contiguous air parcels might contain very different concentrations of species such as NO, NO_2, ClO, HCl and OH. A more detailed analysis should consider the time history of particular air parcels and should include an integration of the appropriate chemical and dynamical equations. This analysis would allow one to address issues relating to the stability of the various possible states, and should identify the state or states favored under prescribed conditions. This matter is under current investigation and will be reported later.

The results in Figure 4 suggest that the concentration of various gases may change rapidly as a function of position and time at latitudes above 45° in winter. This phenomenon may account in part for the abrupt change in the spatial and temporal behavior of NO_2 observed above 50° (Noxon, 1975), and suggests that there might be associated changes in ClO and $ClNO_3$. The spatial scale of the transition zone is of some interest in that it may be sufficiently short as to permit differential molecular diffusion of species across its boundary.

Fig.3. Mean concentrations of NO, NO_2, $ClNO_3$, Cl, HCl and OH as a function of ClO number density for 60°N winter conditions at 16 km.

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