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## THE VERTICAL DISTRIBUTION OF SOLUBLE GASES IN THE TROPOSPHERE

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**Abstract.** The thermodynamic properties of several water-soluble gases are reviewed to determine the likely effect of the atmospheric water cycle on their vertical profiles. We find that gaseous HCl, HNO<sub>3</sub>, and HBr are sufficiently soluble in water to suggest that their vertical profiles in the troposphere have a similar shape to that of water vapor. Thus we predict that HCl, HNO<sub>3</sub>, and HBr exhibit a steep negative gradient with altitude roughly equal to the altitude gradient of water vapor. Therefore, ground-based sources of inorganic chlorine, odd nitrogen, and inorganic bromine compounds are not likely to directly affect the stratosphere in the mean. Calculations also show that while SO<sub>2</sub> and NH<sub>3</sub> are significantly affected by the atmospheric water cycle, their abundances may not decrease with altitude as rapidly as does water vapor.

## Introduction

It is believed that trace amounts of highly water soluble gases, such as HCl, HNO<sub>3</sub>, HBr, NH<sub>3</sub>, and SO<sub>2</sub> are present in the lower atmosphere and they may play a major role in the photochemistry of the troposphere [cf., Junge, 1963; Levy, 1972; Crutzen, 1973; Chameides and Walker, 1973] and stratosphere [cf., Crutzen, 1970; Johnston, 1971; McElroy et al., 1974; Stolarski and Cicerone, 1974; Wofsy and McElroy, 1974]. Unfortunately, because the vertical profiles of these gases have not been systematically measured, it is difficult to accurately assess their roles in the present day atmosphere or their potential future impact as pollutants. To help make this assessment, we estimate here the probable tropospheric vertical profiles of HNO<sub>3</sub>, HCl, HBr, NH<sub>3</sub> and SO<sub>2</sub> due to their interaction with the atmospheric water cycle.

The water-vapor mixing ratio in the troposphere typically exhibits a negative gradient from the ground to the tropopause, as shown in Figure 1. This gradient is maintained against eddy mixing processes by condensation, gravitational settling and evaporation of liquid and solid H<sub>2</sub>O. A typical turnover time for a water molecule to cycle into and out of this settling phase is about 1 day throughout the troposphere [Chameides, 1975] short enough compared to the approximate 30 day tropospheric mixing period [Jacobi and Andre, 1963] to maintain the negative H<sub>2</sub>O gradient.

It is likely that extremely water soluble gases behave like water vapor. In fact, Ryan and Mukherjee [1974] have suggested that HCl profiles should follow the H<sub>2</sub>O mixing profile gradient.

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Their arguments were based on the existence of an HCl-H<sub>2</sub>O dimer, but we consider the conclusions independent of the existence of dimers. For instance, Chameides [1975] has argued that HNO<sub>3</sub> should follow the water-vapor mixing ratio gradient, based on the high solubility of the gas in liquid water. In this work, we generalize the more detailed arguments of Chameides [1975] and suggest which species should exhibit this negative gradient and which should not.

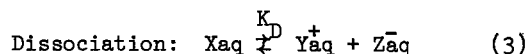
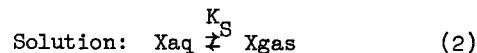
In our discussions we neglect the possible interactions of soluble gases with low pH aerosols [e.g., Robbins et al., 1959]. However, these interactions are not likely to be significant for highly soluble gases since the surface area of liquid and solid H<sub>2</sub>O in the atmosphere is so much larger than that of aerosols. We also neglect irreversible reactions between soluble gases within the cloud droplet, such as the formation of NH<sub>4</sub>Cl. The effect of these reactions will be to cause the vertical profiles of reactant gases to decay somewhat faster than we predict here.

## General Treatment

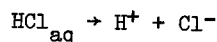
In the process of water condensation, H<sub>2</sub>O vapor and soluble gaseous molecules are transferred to a growing cloud droplet by diffusion at rates approximately proportional to their atmospheric concentrations. (A general discussion of the scavenging of gases by cloud droplets is given by Hales [1972].) A soluble gas X will remain in solution if the vapor pressure Pd(X) of X over a droplet formed by condensing all the H<sub>2</sub>O vapor and X from a given volume is less than the local ambient pressure Pa(X) of X, i.e.,

$$P_a(X) > P_d(X) \quad (1)$$

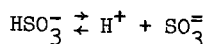
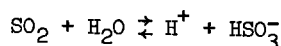
(We will refer to (1) as the condition for total condensation.) If the condition for total condensation is satisfied, then, similar to H<sub>2</sub>O, the amount of gas X that is incorporated into the droplet will be limited by kinetic processes, i.e., molecular diffusion, rather than by equilibrium or thermodynamic processes. The effect of thermodynamic processes is to prevent the gas from escaping from the droplet. The important equilibria in this system are



This dissociative step (3) can be straightforward and complete such as



in which case the solubility constant,  $K_S(\text{atm M}^{-2})$  is given by  $K_S(\text{HCl}) = P(\text{HCl})/[\text{H}^+][\text{Cl}^-]$  where  $P(\text{HCl})$  is the partial pressure of HCl in the gas phase and  $[\text{H}^+]$  and  $[\text{Cl}^-]$  are the concentrations of the ions in solution. However, the dissociative steps can be more complex, such as



in which case the solubility constant  $K_S(\text{SO}_2)$  ( $\text{atm M}^{-1}$ ) is given by  $K_S(\text{SO}_2) = P(\text{SO}_2)/[\text{SO}_2]$ . These dissociative steps can be expressed in a generalized form by introducing a parameter  $\alpha(X)$  where  $\alpha$  represents the effective fraction of X in solution for species not totally dissociated and is simply equal to  $[\text{H}^+]$  for totally dissociated species. Thus,

$$P_d(X) = \alpha(X) [X] K_S(X) \quad (4)$$

where  $[X]$  represents the total concentration, dissociated and undissociated in solution.

The globally averaged pH of precipitation is believed to be about 5.6 and is controlled by the buffering action of  $\text{CO}_2$  with an  $\alpha(\text{CO}_2)$  of 0.82. However, the presence of large amounts of  $\text{H}_2\text{SO}_4$ , HCl, or  $\text{HNO}_3$  in rain is known to significantly lower the pH bringing about acid rain [Granat, 1972]. In these calculations we will restrict ourselves to global average conditions and we therefore assume a pH of 5.6. Using this pH and tabulated thermodynamic values (NBS) to obtain the various  $K_S$ , it is possible to compare the vapor pressure of any gas over a cloud droplet with the ambient pressure of that gas.

If the  $\text{H}_2\text{O}$  partial pressure is  $P(\text{H}_2\text{O})$ , then for total condensation the mole fraction of X in the droplet is given by  $(P_d(X)/P(\text{H}_2\text{O}))$  and therefore

$$[X] = 55 P_d(X)/P(\text{H}_2\text{O}) \quad (5)$$

Substituting (5) into (4),

$$P_d(X) = \alpha(X) K_S(X) 55 P_d(X)/P(\text{H}_2\text{O}) \quad (6)$$

From (1), the condition for total condensation, we find that if

$$\alpha(X) K_S(X) < 0.018 P(\text{H}_2\text{O}) \quad (7)$$

then condensation will remove relatively large amounts of X from the atmosphere into cloud droplets. Thus, subsequent settling and evaporation of the droplets will be an effective downward transport mechanism for X. Provided the photochemical lifetime of X is long compared to the 1 day turnover time for the condensation/evaporation process, this transport mechanism will play the major role in controlling the vertical profile

of X, as it does for  $\text{H}_2\text{O}$ . Thus, it is likely that the vertical profiles of those gases which are relatively long-lived and satisfy condition (7) throughout the troposphere will have the same characteristic shapes as water vapor [Chameides, 1975].

#### Particular Cases

In the case of HCl, from (4) we find that

$$P_d(\text{HCl}) = [\text{H}^+][\text{Cl}^-]K_S(\text{HCl}) \quad (8)$$

Note that in this case, and for all completely dissociated species,  $\alpha(\text{HCl}) = [\text{H}^+] = 2.5 \times 10^{-6}$ , assuming a pH of 5.6. It follows from (7) that the condition for water control of HCl is

$$2.5 \times 10^{-6} K_S(\text{HCl}) < 0.018 P(\text{H}_2\text{O}) \quad (9)$$

At the bottom of the troposphere,  $P(\text{H}_2\text{O}) = 0.02$  atm and  $K_S(\text{HCl}) = 5 \times 10^{-7}$   $\text{atm M}^{-2}$  for  $T = 298^\circ\text{K}$ . These values easily satisfy condition (9).

Table I lists results of similar calculations for several gases assuming lower tropospheric conditions (pH = 5.6,  $T = 298^\circ\text{K}$ ). Note that each gas included in Table I is believed to have a photochemical lifetime of several days or more and is therefore a candidate for water control.

Table I shows that gases such as  $\text{HNO}_3$ , HCl, and HBr are sufficiently soluble in water to have their altitude profiles completely controlled by the atmospheric water cycle.  $\text{SO}_2$  and  $\text{NH}_3$ , on the other hand, are borderline cases in which  $P_d$  and  $P_a$  will be approximately equal. For these molecules, while the condensation process should represent a large sink causing a negative gradient in their mixing profiles, the gradient should not be as steep as that of water vapor. Finally, less soluble species such as  $\text{CO}_2$ , CO, and  $\text{N}_2\text{O}$  are not significantly affected by condensation processes, as confirmed from their observed constant-with-altitude mixing ratio profiles in the troposphere [e.g., Pressman and Warneck, 1970].

It appears that these results are generally applicable for the entire troposphere. For instance, note that solubility constants increase with decreasing temperature. Furthermore, while the arguments presented above were limited to the liquid phase, they probably also apply to the solid ice phase. HCl,  $\text{HNO}_3$ , and HBr can be trapped in ice crystals by rapid freezing of initially supercooled water solutions and possibly through adsorption and burial. The fact that the concentration of acid nitrate and chloride in both rain and snow is equal [G. Likens, personal communication, 1975] suggests that the transport by ice of gases, such as HCl,  $\text{HNO}_3$ , and HBr that have a high affinity for  $\text{H}_2\text{O}$  is as efficient as the transport of these gases by water droplets. The turnover time of  $\text{H}_2\text{O}$  vapor through the solid or liquid phase is about 1 day in the upper troposphere as well as the lower troposphere [Chameides, 1975], as evidenced by the steep negative  $\text{H}_2\text{O}$  density gradient throughout the troposphere. Thus, vertical transport via ice formation controls the profile of  $\text{H}_2\text{O}$  and probably also HCl,  $\text{HNO}_3$ , and HBr in the upper troposphere just as efficiently as liquid water does in the lower troposphere.

Table I.

Water vapor control criteria in the lower troposphere for the altitude profiles of various molecules. If  $\alpha K_s < 1.8 \times 10^{-4}$  then water vapor control will be effective. Temperature 298°K, droplet pH 5.6.

Molecule	$K_s^*$	$\alpha$	$\alpha K_s$	Water Vapor Control
HBr	$2 \times 10^{-9}$	$2.5 \times 10^{-6}$	$5.0 \times 10^{-15}$	Yes
HNO <sub>3</sub>	$4 \times 10^{-7}$	$2.5 \times 10^{-6}$	$1.0 \times 10^{-12}$	Yes
HCl	$5 \times 10^{-7}$	$2.5 \times 10^{-6}$	$1.3 \times 10^{-12}$	Yes
SO <sub>2</sub>	0.8	$1.7 \times 10^{-4}$	$1.4 \times 10^{-4}$	Borderline
NH <sub>3</sub>	$1.7 \times 10^{-2}$	$2.2 \times 10^{-4}$	$3.7 \times 10^{-4}$	Borderline
N <sub>2</sub> O	20	1	20	No
CO <sub>2</sub>	30	0.85	25	No
CO	$10^3$	1	$10^3$	No

\* $K_s$  has units of  $(\text{atm})(\text{M})^{-2}$  for HBr, HNO<sub>3</sub>, and HCl and  $(\text{atm})(\text{M})^{-1}$  for all others.

From these considerations, we propose that the vertical profiles of gaseous HCl, HNO<sub>3</sub> and HBr, similar to H<sub>2</sub>O, are controlled by water condensation/evaporation in the lower troposphere and by water freezing/sublimation in the upper troposphere. Thus it is likely that the vertical profiles of tropospheric HCl, HNO<sub>3</sub>, and HBr are similar in shape to that of H<sub>2</sub>O, with steep negative gradients with altitude. In other words, the density  $n_x$  of these gases as a function of altitude  $z$  is given by  $n_x(z) = A_x \cdot n(\text{H}_2\text{O})(z)$ , where  $A_x$  is the volume mixing ratio between X and H<sub>2</sub>O.

In Figure 1 we predict average vertical profiles for HCl and HNO<sub>3</sub>. For comparison the average profiles of water vapor [July and January U.S. Standard Atmosphere Supplements, 1966, at 30°N] and CO [Pressman and Warneck, 1970] are also shown. The HCl profile was obtained by assuming a ground-level mixing ratio near 1 ppb, from the measurements of Junge [1957], Duce et al. [1965], Duce [1969], and Chesselet et al. [1972]. (We note however, that this value may be an upper limit because of the possibility of particle-to-gas conversion in their inlet systems. Possible opposing errors in these measurements due to HCl absorption are probably not very large, as the authors noted). Nevertheless, assuming total condensation, a  $10^{-9}$  atmospheric mixing ratio for HCl implies a  $10^{-7}$  volume mixing ratio of HCl to H<sub>2</sub>O (i.e.,  $A_{\text{HCl}} = 10^{-7}$ ). This is roughly consistent with the average chloride concentration in rain at rural inland stations in the northeastern U. S. [Pearson and Fisher, 1971]. No direct measurements of tropospheric profiles are available to compare with Figure 1, but Farmer et al. [1974] have indicated, from ground-based spectroscopic data, that HCl diminishes rapidly with altitude, possibly with a 3 km scale height. Lazrus et al. [1975] find less than 0.05 ppb HCl near 14 km and rapidly increasing concentrations with altitude above. These results indicate a stratospheric source of HCl and support our contention of a water controlled HCl profile throughout the troposphere [Cicerone et al., 1975].

The profile of HNO<sub>3</sub> shown in Figure 1 was obtained similarly. Since the tropospheric abundance of HNO<sub>3</sub> has not been measured, we determine the ground level HNO<sub>3</sub> mixing ratio from the average concentration of nitrates in rainwater. This concentration, about  $2 \times 10^{-5}\text{M}$  [Eriksson, 1952; Pearson and Fisher, 1971] implies that  $A_{\text{HNO}_3} = 4 \times 10^{-7}$  [Chameides, 1975] assuming all nitrates in rain are formed from the absorption of gaseous HNO<sub>3</sub>. This is a reasonable assumption since HNO<sub>3</sub> is the most soluble as well as the most abundant of the odd nitrogen gases in the troposphere.

The HBr profile, which we predict to be similar in shape to H<sub>2</sub>O also, is not shown in Figure 1 due to the lack of accurate measurements of its ground-level concentration or of the bromide concentration in rainfall.

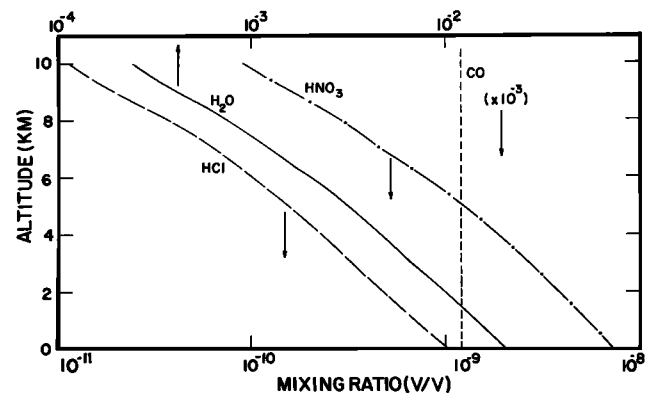


Figure 1. The mixing ratio profiles of H<sub>2</sub>O, HCl, HNO<sub>3</sub>, and CO. The H<sub>2</sub>O profile is represented by the solid line, with the top abscissa and is the average of the July and January U.S. Standard Atmosphere Supplements [1966] at 30°N. The predicted HCl and HNO<sub>3</sub> profiles are represented by the broken and dash-dotted lines, respectively, with the bottom abscissa. The CO profile is represented by the dashed line with the bottom abscissa and is taken from Pressman and Warneck [1970].

Recall for the borderline cases, SO<sub>2</sub> and NH<sub>3</sub>, it is likely that the shapes of their vertical profiles are intermediate between the rapid decrease of HCl or HNO<sub>3</sub> and the constant mixing ratio profile of CO, CO<sub>2</sub>, or N<sub>2</sub>O. Qualitatively consistent with this result is Kaplan's [1973] spectroscopic measurement of NH<sub>3</sub> in the upper troposphere that shows less than 10<sup>-2</sup> that of NH<sub>3</sub> near the ground.

#### Conclusion

Calculations show that the mixing ratio profiles of HCl, HNO<sub>3</sub>, HBr, NH<sub>3</sub>, and SO<sub>2</sub> are significantly affected by the tropospheric H<sub>2</sub>O condensation/evaporation and freezing/sublimation cycles. While the abundances of HCl, HNO<sub>3</sub> and HBr are likely to decrease with altitude at about the same rate as that of water vapor, NH<sub>3</sub> and SO<sub>2</sub> probably do not decrease as rapidly. Since the profiles of HCl and HNO<sub>3</sub> essentially determine the profiles of inorganic chlorine and odd nitrogen compounds, respectively, ground-based sources of these species should not directly affect the stratospheric photochemical system. The same is likely true for bromine, as well as NH<sub>3</sub> and SO<sub>2</sub>. These predictions are directly testable by accurate measurements of these species in the troposphere.

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