

## NITRIC ACID AEROSOLS AT THE TROPICAL TROPOPAUSE

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**Abstract.** It is thermodynamically possible for nitric acid aerosol particles to form in the lower stratosphere and upper troposphere in tropical latitudes. This aerosol would have essentially the same composition as the polar stratospheric clouds observed in the winter polar stratosphere. We have carried out calculations indicating that nitric acid aerosols may form at the same altitudes as layers observed in the tropics by the SAGE satellite system.

## Introduction

Toon et al. (1986) and Crutzen and Arnold (1986) showed that in the winter, the stratosphere over Antarctica is cold enough for frozen nitric acid/water solution particles to form. Recent observations (such as those by Poeschel et al., 1988) suggest that "Type I" polar stratospheric clouds are indeed composed of nitric acid. These aerosols are of considerable interest because they may be related to the springtime ozone depletion and the formation of the ozone hole. In this paper, we show that frozen nitric acid aerosol particles can also form in the lower tropical stratosphere. We outline a simple microphysical model to account for the growth and sedimentation of these particles. We show that growth/evaporation processes can lead to the development of particulate layers in the regions where the environmental temperature is cold enough.

## Thermodynamic Considerations

Nitric acid vapor is present in the stratosphere at a concentration which varies with latitude from about 5 ppbv in the polar regions to about 1 ppbv in the tropics (Austin et al., 1986). Hanson and Mauersberger (1988) recently measured nitric acid and water vapor pressures over frozen solutions at the eutectic compositions of 70% and 32.3% HNO<sub>3</sub> (by weight). According to the Clausius-Clapeyron equation the log pressure vs inverse temperature curve should be a straight line.

At very low temperatures the 32.3% data of Hanson and Mauersberger show considerable variability around a straight line fit; this is probably due to variations in

the composition of the solution. Hence, there is uncertainty in a straight line extrapolation of the data. Nevertheless, such an extrapolation of the ice/hydrate vapor pressure indicates that a 32.3% HNO<sub>3</sub> solid solution at 192 K has a nitric acid vapor pressure less than 10<sup>-7</sup> mb and a water vapor pressure less than 5X10<sup>-4</sup> mb. At 100 mb altitude (about 16 km), 1 ppbv of HNO<sub>3</sub> corresponds to a partial pressure of 1 X 10<sup>-7</sup> mb. For a water concentration of 5 ppmv, the H<sub>2</sub>O partial pressure will be 5 X 10<sup>-4</sup> mb. Therefore, relative to a 32.3% solution, a cold stratospheric environment is saturated in both water and nitric acid and the formation of frozen nitric acid/water particles can take place.

In the preceding discussion, we considered a 32.3% solution because data exist for such a system; however, the actual weight percentage of nitric acid in an aerosol particle depends on the environmental condition. As indicated by Hanson and Mauersberger, the composition of the frozen solution is variable. Some researchers suggested that the nitric acid particles would form at the hydrate compositions. However, Hamill, Turco and Toon (1988) showed that this does not agree with the temperatures at which the particles are observed to form in the Antarctic stratosphere, whereas amorphous frozen particles of a variable composition would form at the observed temperatures. Hence, in this paper we shall assume that the particles are solid solutions having a variable composition. Actually, for the conditions expected at the tropical tropopause, the nitric acid droplets will have weight percentages quite near the 32.3% eutectic, so the fact that the particles may have a variable composition has very little effect on the results presented here.

The growth of a variable composition solution particle is governed by a mechanism known as heteromolecular condensation which is discussed by Steele and Hamill (1981). This mechanism is based on the fact that the vapor pressure of a solution droplet depends on its composition. If the environment is supersaturated with respect to both nitric acid and water, a solution particle will absorb or evaporate enough water to come into equilibrium with the water (because water is the more abundant of the two species). The particle will subsequently grow by absorbing the nitric acid molecules which impinge upon it; for each nitric acid molecule absorbed, the particle absorbs as many water molecules as required to maintain equilibrium with respect to water. During the growth process, the particle will maintain a composition such that its water vapor pressure is equal to the environmental water partial pressure.

We have used calculated values for the vapor pres-

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tures of  $\text{HNO}_3$  and  $\text{H}_2\text{O}$  over solution particles with the composition of the eutectics to obtain an approximate expression valid for compositions from 20% to 80% by weight  $\text{HNO}_3$ . The values of the vapor pressures obtained with the empirical relation agrees quite well with the values obtained by Hanson and Mauersberger for the 32.3% eutectic, but are somewhat high for the 70% eutectic. Since the analysis in this paper is concerned with low values of nitric acid, we feel that the vapor pressures are sufficiently well represented by the following empirical relations:

$$VP_{\text{HNO}_3} = \exp[-(8580 - 24.08 W)/T + 0.082 W + 19.8]$$

$$VP_{\text{H}_2\text{O}} = \exp[-(5650 + 29.63 W)/T + 0.095 W + 23.0]$$

where  $W$  is the weight percentage nitric acid of the solution and  $T$  is the temperature in kelvin. The vapor pressures are given in torr.

### Observations

The very low temperature required for the formation of nitric acid particles is reached in the stratosphere in the polar regions during the winter season and at the tropical tropopause during all seasons. In the polar regions, the cold temperatures are associated with the formation of the polar stratospheric clouds which have been observed by the SAM II satellite system (McCormick et al., 1982) as well as by air borne lidar (Kent et al., 1986). The SAM II data indicate that polar stratospheric clouds are most prevalent when the temperature is below about 194 K and are very seldom observed when the temperature is greater than about 197 K. According to Newell et al. (1974), at the equator at 100 mb, the average temperature ranges from 192 K to 198 K. Therefore, if sufficient  $\text{HNO}_3$  is present, cloud formation should occur. Observational evidence of nitric acid clouds in the tropics has not been discussed in the literature, but there is evidence in the published SAGE satellite aerosol data (McCormick, 1985) of regions of high extinction in the tropical lower stratosphere and upper troposphere. The satellite data show that the highest values of the average weekly extinction ratio profiles are in the  $10^\circ$  N to  $10^\circ$  S latitude band with maximum values of extinction ratio frequently exceeding twice the maximum value at mid latitudes. (The extinction ratio is the ratio of measured extinction at 1.00 micron wavelength to the calculated molecular extinction at the same altitude and wavelength.) In Figure 1 we plot the average extinction ratio and average temperature profile for measurements made between  $0^\circ$  and  $10^\circ$  S during March of 1979 as given in the SAGE data compilation by McCormick. During this period in the tropical latitudes the background stratospheric aerosol layer was above 20 km and had an extinction ratio of about 4. The profile shown in the figure is a composite of all measurements made in the latitude band and it is to be expected that in some individual measurements there is a larger peak in extinction ratio and in others the extinction ratio is smaller. The maximum in the extinction ratio profile indicates a particle layer peaked at

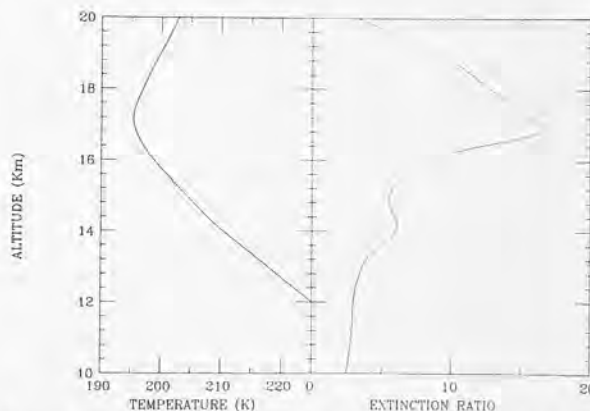


Figure 1. Average temperature and extinction ratio profiles from the SAGE satellite data taken between  $0^\circ$  and  $10^\circ$  South during March, 1979.

about 17 km at the minimum in temperature. Clearly, there is a layer of particulates at the tropopause. The temperature profile indicates that it is not cold enough for pure water to condense. Although only *in-situ* measurements can determine the nature of the particles, in this paper we suggest that this region of enhanced extinction may be due to the formation of nitric acid aerosols.

The temperature profile of Figure 1 suggests a stable atmosphere since the lapse rate is sub-adiabatic; however, it is must be kept in mind that this is an average temperature profile obtained from the calculated temperature profiles for all of the satellite measurement points in a given latitude band. It is possible that the aerosol layer illustrated in the figure may be due to particle-laden tropospheric air mixed upwards. Since the averaging process will obscure temperature excursions below the frost point, we cannot rule out the possibility that the high extinctions are due to thin cirrus clouds. However, the SAGE extinction profiles frequently indicate aerosol layers somewhat above the tropopause. If we assume stratospheric water vapor concentrations, the temperatures are too high for cirrus clouds to form. The fact that the air below the tropopause is frequently aerosol-free implies the layers are due to local formation of aerosols rather than by vertical transport. The appearance of the layers at the altitude predicted by vapor pressure considerations suggests that it is plausible that some of these high extinction events are due to nitric acid condensation.

### Description of the Model

To explore the behavior of nitric acid aerosol particles in the lower tropical stratosphere, we have developed a simple numerical model which incorporates the principal physical mechanisms which will affect the aerosol. The model assumes particle growth by heteromolecular condensation. As a particle grows, it falls due to gravitational sedimentation. Since the temperature

will normally increase with decreasing altitude, a falling particle will eventually reach a point at which it begins to evaporate. Depending on the evaporation rate and on the updraft, the particle will either evaporate completely or will grow small enough to be transported aloft once again. At higher altitudes, it may begin growing and eventually be large enough to fall, thus undergoing a cycle in which it absorbs water and nitric acid above the evaporation level and deposits these gases below the evaporation level.

A nitric acid/water solution should quickly come to equilibrium with the environmental water vapor. This implies that the  $H_2O$  vapor pressure of the particle will be equal to the environmental  $H_2O$  partial pressure. Such an equilibrium is obtained by the particle absorbing or evaporating water molecules until it reaches an equilibrium composition. Our calculations indicate that for the conditions expected near the tropical tropopause, the equilibrium composition will range from about 27% to 35%  $HNO_3$  (by weight). This is less than the expected nitric acid weight percentage for the polar stratospheric clouds because the nitric acid concentration is much lower in the tropical stratosphere than in the polar stratosphere.

In our analysis, the environmental nitric acid concentration was usually assumed to be 1 ppbv. In several of the model runs this parameter was varied to study the effect of larger and smaller nitric acid concentrations on the behavior of the particle. The water vapor concentration was always constrained to be less than the vapor pressure of water over ice (as evaluated using the Goff-Gratch formula given in List, 1958). This was done because it is expected that in the real atmosphere, whenever saturation with respect to ice is reached, ice crystals will form and will fall rapidly. In our calculations, we usually assumed that the water concentration was 5 ppmv.

### Results

We carried out our calculations using various sets of initial conditions and different values of temperature and nitric acid and water concentrations. We now discuss the results obtained.

In Figure 2 we plot particle growth as a function of time assuming the number of particles formed per  $cm^3$  is 1, 0.1 and 0.01. The assumed environmental conditions were  $T = 194$  K,  $[HNO_3] = 1$  ppbv, and  $[H_2O] = 5$  ppmv. As indicated in the figure, particle growth is quite rapid, the final size being reached in a number of hours. If fewer particles are nucleated, the final radius is greater because the available nitric acid is shared among fewer particles. For the case of 1 particle per  $cm^3$ , the final particle size is about  $0.3 \mu m$ , a value which yields an extinction in agreement with the SAGE observations. In the remainder of this paper, we assume a particle number density of  $1/cm^3$ .

Model runs at different values of environmental temperature indicate that for 1 ppbv  $HNO_3$  and 5 ppmv

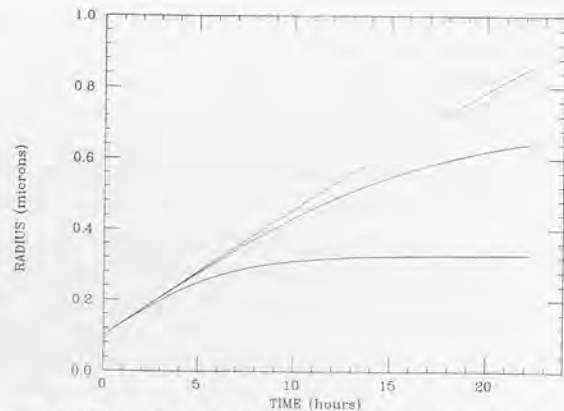


Figure 2. Growth rate of nitric acid/water solution particles at 17 km altitude, 194 K,  $[HNO_3] = 1.0$  ppbv, and  $[H_2O] = 5$  ppmv. The top curve is for 0.01 particle/ $cm^3$ , the middle curve assumes 0.1 particle/ $cm^3$  and the bottom curve is for 1 particle/ $cm^3$ .

$H_2O$ , particle formation will occur at temperatures less than about 194 K. At higher temperatures, the particles evaporate (unless, of course, the nitric acid concentration is higher). The lower the temperature, the larger the particles will be. This is due to the fact that the composition depends on the temperature and at colder temperatures the particles are more dilute. For example, for the conditions given above, the radius varies from  $0.32 \mu m$  at 194 K to  $0.62 \mu m$  at 190 K.

The effect of varying  $HNO_3$  and  $H_2O$  concentrations is shown in Figure 3. The solid curve shows the particle

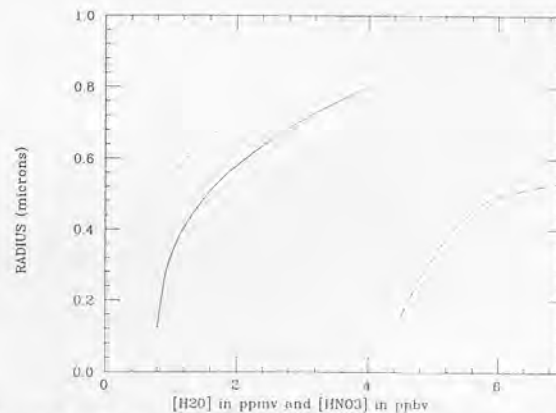


Figure 3. Radius of nitric acid/water solution particles at 17 km altitude for different values of environmental water vapor and nitric acid after a growth time of 50,000 sec. The scale gives concentration in ppbv for nitric acid and in ppmv for water. The solid curve shows the radius as a function of nitric acid concentration, assuming 5 ppmv water and a temperature of 194 K. The dashed curve shows the radius as a function of water concentration assuming 1 ppbv nitric acid and temperature of 194 K. The dotted curve also gives the radius as a function of nitric acid concentration for 5 ppmv water but for a colder temperature of 192 K.

radius as a function of  $\text{HNO}_3$  concentration assuming 5 ppmv water and 194 K. This shows that as long as the nitric acid concentration is greater than about 0.8 ppbv, the particles will form. The greater the nitric acid concentration, the larger the particles will be. The effect of changing water concentration is shown by the dashed curve of the same figure, and it indicates that if the water vapor concentration is less than about 4 ppmv, the particles cannot form. These curves are temperature dependent, and for lower temperatures the particles can form at lower concentrations of nitric acid and water concentration. This is illustrated by the dotted curve which is also for 5 ppmv of water but evaluated at a temperature of 192 K. Note that the particles now form at a nitric acid concentration of about 0.4 ppbv. The formation temperature also has a small dependence on altitude (or total pressure).

It is interesting to note that regardless of their initial size, for the same environmental conditions, the particles all tend to grow to essentially the same radius (as is characteristic of condensational growth processes). This indicates that the nitric acid layers will have a nearly monodisperse size distribution.

We have also carried out calculations for particles falling from different initial altitudes in the presence of a small, steady updraft. These calculations indicate that during extended periods of steady state updraft and temperature profiles, the aerosol particles tend to fall to the evaporation level where they form narrow strata with a monodisperse size distribution. It would appear that evaporation/condensation processes can be responsible for the formation of such narrow layers. It is interesting but not surprising that the altitude of these layers is determined by the temperature profile and the final size of the particles is determined by the updraft profile.

**Acknowledgments.** P.H. acknowledges support from NASA grant NASW-4160 and G. F. acknowledges support from Piano Spaziale Nazionale, Ministero Pubblica Istruzione and Programma Antartide. This work was carried out at the University of Rome where P.H. spent a sabbatical semester.

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(Received: July 22, 1988;

Accepted: August 12, 1988.)