CONDENSATION OF HNO₃ AND HCl IN THE WINTER POLAR STRATOSPHERES

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Abstract. Nitric acid and hydrochloric acid vapors may condense in the winter polar strato- spheres. Nitric acid clouds, unlike water ice clouds, would form at the temperatures at which polar stratospheric clouds (PSCs) are observed and would have optical depths of the magnitude observed suggesting that HNO₃ is a dominant com- ponent of PSCs. ClO, N₂O₅ and ClNO₃ may react on cloud particle surfaces yielding additional HNO₃, HCl, and HOCL. In the vicinity of PSCs these reactions could deplete the stratosphere of photochemically active NO_x species. The sedi- mentation of PSCs may remove these materials from the stratosphere. The loss of vapor phase NO_x might allow halogen-based chemistry to create the ozone hole.

Introduction

Satellites have observed persistent, optically thin clouds in the polar twilight at temperatures near the frost point of water (McCormick et al., 1982). HNO₃ and HCl can condense as aqueous aerosols in the winter polar stratosphere and are thus the third and fourth substances (in addition to water and sulfuric acid) which have been recognized as being able to undergo condensation and evaporation cycles in the Earth's atmo- sphere. This condensation process may play an important role in the formation of polar strato- spheric clouds (PSCs), it may act as a sink for stratospheric nitrogen oxides, and it may influ- ence the chemistry which creates the Antarctic ozone hole.

Partial Pressures of HNO₃ and HCl

Figure 1 shows the partial pressures of nitric acid solutions. The vapor pressure of pure water has been measured down to 195 K. Its logarithm is a linear function of the inverse temperature with a slope change at the melting point (Jancso et al., 1970). The vapor pressure of pure nitric acid has been measured down to 263 K (Duisman and Stern, 1969). We extrapolated this vapor pres- sure curve to the melting point by maintaining the slope. Below the melting point we extrapo- lated to 190 K using the Clausius-Clapeyron equa- tion and the latent heat of fusion of nitric acid to determine the new slope (Forsythe and Giaque, 1942). The partial pressures of solutions have been measured down to 273 K (Clavelin and Mirabel, 1979). We extrapolated these pressures by maintaining constant slopes down to the melt- ing points. In one case (solid curves) we alter the slopes of the partial pressure curves below

the melting points in proportion to the la[t] heat of the pure material (either water HNO₃). In another case (dashed curves) slopes were obtained by using the latent heat[s] fusion for the monohydrate (77.77%) and tri drate (53.8%). The correct partial pressures lie between these cases.

There is a considerable degree of uncerta[inty] in extrapolating the vapor pressures to temperatures found in the polar stratosph[ere] Nevertheless, the nitric acid trihydrate is s[atu] rated with respect to both nitric acid and wa[ter] vapor in the temperature range of 190 K [-] 200 K. The trihydrate has about half the w[ater] partial pressure that pure ice has at the [same] temperature and would condense at more than [ ] higher temperatures than pure ice would. [ ] lower temperatures, more dilute solutions w[ould] be saturated. Such solutions will be frozen strongly supercooled (Kirk and Othmer, 1981).

Figure 2 illustrates the partial pressure[s] HCl solutions for temperatures greater than 27[ ] (Perry, 1984) and temperatures in the range [ ] 273 K to 238 K (Miller, 1983). At 273 K th[e] two data sets agree with respect to the magni[tude] of the partial pressure at that point. Howe[ver] for HCl the slopes of the curves do not match all concentrations. Because of the uncerta[inty] in the slopes of the partial pressure curves the liquid, we have not altered the slope at melting point. Frozen solutions would have l[ower] partial pressures than would liquid ones. [ ] melting points of solutions less concentr[ated] than 20% suggest that HCl solutions would frozen in the winter polar stratosphere.

The abundance of HCl in the polar stratosph[ere] is sufficient to cause the condensation of an[ ] solution whose concentration is less than [ ] The partial pressure depression of water in [ ] solutions would allow condensation at tempe[ra] tures which are slightly higher than those pure ice.

We are not aware of any data relating to [ ] partial vapor pressures or freezing points mixtures of water, HNO₃, HCl and sulfuric acid

Effect of Condensation on Vapor Phase Abundances of HNO₃ and HCl

The condensation of HNO₃ and HCl would lead[ ] rapid and quantitatively significant depletion[ ] these acids in the vapor phase.

The inverse of the e-folding time-constant removal of molecules from the vapor phase roughly the product of the molecular ther[mal] velocity (2×10⁴ cm s⁻¹ for HNO₃, 3×10⁴ cm s⁻¹ HCl) and the cloud surface area per unit v[ol] ume. The surface area is $4k/Q_e$. Here k the measured extinction coefficient and Q_e is the extinction efficiency (for large p[ar] ticles). We find that PSCs present surface a[rea]
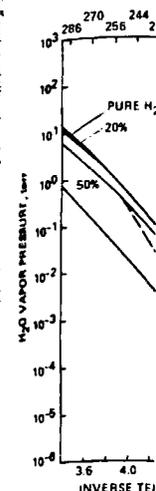

Fig. 1. The nitric acid weight perce[nt] bars corresp[ond] spheric temp[ ] Remsberg et [ ] et al., 1984) 20 km.

ranging fro[m] 5×10⁻⁷ cm²/cm time for dep[osition] PSCs is twent[y] The rapid [ ] in the conden[sation] that the pres[ ] to the parti[ ] slopes of th[ ] that, as the at which con[ ] 195 K at 2[ ] observed (abo[ve] and HNO₃ coul[d] of magnitude. by numerical process since functions of water vapor concentration ature decreas[es] The acid [ ] tributed as northern hem[i] (McCormick e[t] clouds evapor[ ] to the vapor are much m[ ] hemisphere (M[ ] tude of the through the particles are downward by [ ] 2 to 5 km mo[ ] Hence, partic[ ] resulting in of the HNO₃, vortex during partly comper[ ] fresh HNO₃, stratosphere, latitudes.
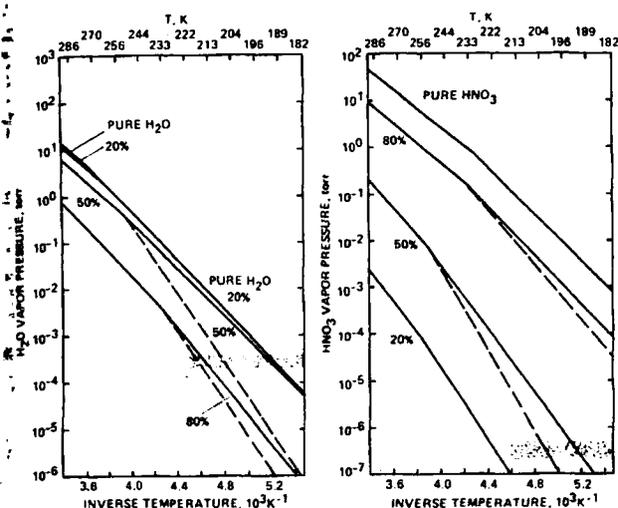
Fig. 1. The partial pressures of water (a) and nitric acid (b) above solutions having various weight percentages of nitric acid. Horizontal bars correspond to the range of ambient stratospheric temperatures, water vapor (5 ppmv, Remsberg et al., 1984) and HNO₃, (5 ppbv, Gille et al., 1984) pressures at altitudes from 15 to 20 km.

ranging from 10^{-8} cm²/cm³ to more than 5×10^{-7} cm²/cm³. Therefore, the characteristic time for deposition of HNO₃ and HCl vapors on PSCs is twenty minutes or less.

The rapid deposition of the vapor will result in the condensation of an amount of vapor such that the pressure of the remaining vapor is close to the partial pressure of the solution. The slopes of the partial pressure curves suggest that, as the temperature declines from the point at which condensation might first occur (about 195 K at 20 km) to the lowest temperature observed (about 180 K), the concentrations of HCl and HNO₃ could be reduced by more than one order of magnitude. This estimate needs to be refined by numerical simulations of the condensation process since the partial pressures are strong functions of the solution concentration. The water vapor abundance determines the solution concentration and it also declines as the temperature decreases and condensation proceeds.

The acid sequestered in clouds can be redistributed as the cloud particles fall. In the northern hemisphere the PSCs are short lived (McCormick et al., 1982). Therefore, as the clouds evaporate, the condensed acid is returned to the vapor phase locally. However, the clouds are much more persistent in the southern hemisphere (McCormick et al., 1982). The altitude of the cloud layer is observed to decline through the winter season suggesting that the particles are falling, or are being transported downward by a vertical wind, at a rate of about 2 to 5 km month⁻¹ (Hamill and McMaster, 1984). Hence, particles may move across the tropopause resulting in the loss of a significant fraction of the HNO₃, HCl, and H₂O in the Antarctic polar vortex during winter. Atmospheric motions may partly compensate for this removal by bringing fresh HNO₃, HCl, and H₂O into the polar stratosphere, either from aloft, or from other latitudes. Measurements show an Antarctic

"aerosol hole" in October (Hamill and McMaster, 1984), suggesting net removal of particles from the vortex during the winter season.

Although the Antarctic vortex may become depleted in HNO₃, HCl, and H₂O, it is dynamically isolated from the rest of the stratosphere, limiting the amount of acid that is removed to a small fraction of that which is present in the global stratosphere. It is estimated that particle sedimentation in PSCs accounts for less than 1% of the net removal of water from the stratosphere (Hamill and McMaster, 1984). Similar figures could apply for the efficiency of the PSCs as sinks for global stratospheric HNO₃ and HCl.

Composition of Polar Stratospheric Clouds

It was previously thought that PSCs are composed of water ice and a small amount of sulfuric acid (Hamill and McMaster, 1984). We find that the extinction coefficients of PSCs and the temperatures at which they first form are consistent with clouds composed predominantly of concentrated solutions of nitric acid.

PSCs have been defined as clouds in which the extinction coefficient observed by the SAM II satellite at a wavelength of 1 μm is greater than 8×10^{-4} km⁻¹ (McCormick et al., 1982). Of the 538 clouds observed in 1979, more than 50% had extinctions less than 3×10^{-3} km⁻¹, and only 10% had extinctions greater than 10^{-2} km⁻¹ (McCormick et al., 1982). If temperatures drop about 4 K below the condensation point, about 2.5 ppmv of water would be transferred to the condensed phase. As indicated in Table 1, water ice clouds containing 2.5 ppmv of water and composed of micron-sized particles have much larger extinction coefficients than 10^{-2} km⁻¹. Water ice clouds containing particles large enough (>10 μm) to produce the observed extinction have fall velocities in excess of 1 km day⁻¹, much higher than observed (McCormick et al., 1982).
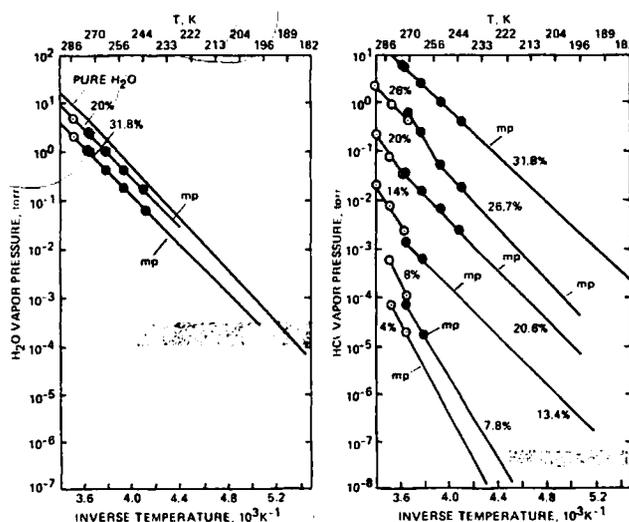

Fig. 2. The partial pressures of water (a) and HCl (b) above solutions having various weight percentages of hydrochloric acid. The melting points are designated by the symbol, mp. The horizontal bars correspond to the range of ambient stratospheric temperatures, water (5 ppmv) and HCl (1 ppbv, Solomon and Garcia, 1984) pressures.

TABLE 1. Potential Extinction of Cloud Constituents

Altitude (km)	Extinction (km^{-1})[a]			
	H$_2$SO$_4$	HNO$_3$	HCl	H$_2$O
15	6×10^{-4}	1×10^{-2}	3×10^{-3}	0.5
20	1×10^{-4}	6×10^{-3}	2×10^{-3}	0.3

[a]The extinction was estimated from 3MQ$_e$/4dr. The condensed mass, M, was assumed to be equivalent to 0.2 ppbv, 5 ppbv, 1 ppbv, and 2.5 ppmv for H$_2$SO$_4$, HNO$_3$, HCl, and H$_2$O, multiplied by 2 for a 50% HNO$_3$ solution and 5 for a 20% HCl solution. Q$_e$ is 2, d is 1 gm cm^{-3}. For HNO$_3$ and HCl the radius, r, is 0.5 μm, but for H$_2$O it is 1 μm, implying about 2 particles cm^{-3} as observed. For H$_2$SO$_4$ we simply multiplied the observed extinction by the mass increase as the solution changed from 75% to 20%.

Correlations between cloud opacity and temperature have been made by interpolating data obtained from other sensors to the locations of the clouds seen by the SAM II instrument. Temperatures at the location of maximum extinction were not low enough for condensation to occur with water vapor concentrations of 5 ppmv for any of the Northern Hemisphere clouds observed by McCormick et al. (1982). Generally, the temperatures were from 3 to 6 K too high for condensation. In the Antarctic, Steele et al. (1983) found a large number of clouds within about 5 K above the condensation temperature. The LIMS satellite observations also recorded PSCs, as well as water vapor and temperature (Hamill and McMaster, 1984). These data show that the temperatures were a few degrees too high for the ambient water vapor to condense. Although the temperature discrepancies are small, they are suggestive of a difficulty with the interpretation that PSCs are composed of water ice.

As an alternative to previous ideas, we use the information in Table 1 to derive a conceptual model of PSCs formed from nitric acid.

As the stratospheric temperature declines to about 200 K, the ambient aerosols will absorb water vapor (Steele et al., 1983). The most dilute solution likely to occur before the formation of relatively pure water ice is composed of at least 20% H$_2$SO$_4$. Except after large volcanic eruptions this aerosol has an extinction coefficient well below that of PSCs.

At temperatures below 200 K, nitric acid and hydrochloric acid will condense on the sulfuric acid droplets. Since the masses of sulfuric acid and of hydrochloric acid in the stratosphere are an order of magnitude less than that of nitric acid, the sulfuric and hydrochloric acids will be minor components of the particles. (Following the El Chichon eruption H$_2$SO$_4$ was temporarily comparable to HNO$_3$). The extinction of the resulting clouds of nitric acid trihydrate will lie in the range observed for PSCs and the particle size will be about 0.5 μm. As the temperature drops closer to the condensation point for pure water, the droplets will become more dilute, and larger. Droplets larger than 1 μm are needed before the particles can remove appreciable

material from the stratosphere by sedimentation during the winter.

As the temperature drops below the condensation point for 5 ppmv of water vapor (about 190 at 20 km), a small fraction of the nitric acid particles will rapidly grow into water ice particles tens of microns in size (Heymsfield, 1986). These large particles will have fall velocities in excess of 1 km day^{-1} and will settle to lower altitudes, taking most of the ambient water and some HNO$_3$ with them. The removal of water vapor will cause the stratosphere to remain barely saturated with respect to ice at the ambient temperature. The majority of the nitric acid particles, which constitute the long-lived PSCs at these temperatures, will exist as unactivated aerosols (Pruppacher and Klett, 1978). The size and the solution concentration of these aerosols is difficult to predict; however, they could be large enough to lead to significant sedimentation over the winter season.

Implications for Stratospheric Chemistry

Condensation of HNO$_3$ and HCl may play a significant role in the formation of the ozone hole. The condensation of HNO$_3$ removes it from the gas phase and thereby reduces its photolysis rate. The presence of HCl on surfaces may enhance certain reaction rates. Finally, heterogeneous reactions may yield further HNO$_3$ and HCl directly on particle surfaces, potentially converting most of the available vapor phase NO$_x$ into condensed HNO$_3$.

Table 2 summarizes the limited data on heterogeneous reactions. ClO could be converted effectively to HCl by ice clouds. The surface conversion of ClNO$_3$ into HOCl and HNO$_3$ as well as the conversion of N$_2$O$_5$ into HNO$_3$ might be rapid for dense clouds if the reaction dependence of the reaction efficiency is large.

Solomon et al. (1986) proposed that the heterogeneous reaction ClNO$_3$+HCl→HNO$_3$+Cl$_2$, might be a significant source of Cl$_2$. McElroy et al. (1986) argued that the reaction was implausible because

TABLE 2. Surface Reactions on PSCs

Reaction	Efficiency Ω	Time Constant[c]	
		10^{-2} km^{-1}	10^{-3} km^{-1}
N$_2$O$_5$ + H$_2$O → 2HNO$_3$	>3.8×10^{-5}[a] 1×10^{-3}[b]	<100 4	10 0.4
ClNO$_3$ + H$_2$O → HNO$_3$ + HOCl	1×10^{-5}[a] 1×10^{-3}[b]	400 4	40 0.4
ClO + H$_2$O → HCl + ?	3.6×10^{-3} at 200 K[d]	1	0.1

[a]Measured on a 95% H$_2$SO$_4$/5% H$_2$O aerosol at 300 K (Baldwin and Golden, 1979).
[b]Estimated for 200 K using the temperature dependence in e.
[c]The reaction time constant, t (months)= 2/kvΩ. v is taken to be 200 m sec^{-1}. Values given for two extinction coefficients.
[d]On 75% H$_2$SO$_4$/25% H$_2$O surface down to 230 Ω = 3.7×10^{-10} e$^{3220/T}$ (Martin et al., 1980).

required the presence of two minor species simultaneously on the ice surface. However, if the HCl is a constituent of the surface, then the reaction might be rapid. Laboratory data concerning reactions on HNO_3-HCl-H_2O surfaces are needed.

Perhaps the most important chemical role of condensation is to remove HNO_3 from the vapor phase. The abundance of nitrogen oxides is crucial for several theories which propose ozone destruction catalysed by halogen radicals and which depend on the condition that $[ClO]>[NO_2]$ (Solomon et al., 1986; McElroy et al., 1986). The photolysis rate for HNO_3 at 75° S in late September is of the order 10^{-7} sec^{-1}. If there are 5 ppbv of HNO_3 vapor in the stratospheric air, the condition would be violated in about 50 days. If the PSCs do remove HNO_3 from the vapor phase, however, then the constraint can be maintained. After the PSCs disappear from the Antarctic stratosphere toward the end of September, the ozone hole ceases to deepen. Such behavior would be explained by the sequestering of NO_x in the form of condensed HNO_3. It is also possible that sedimentation may lead to the removal of HNO_3 from the stratosphere.

Conclusions

PSCs may be composed of concentrated solutions of nitric acid with lesser amounts of HCl and H_2SO_4. Condensation will act to deplete the Antarctic vortex of H_2O, HNO_3, and HCl vapors, perhaps by as much as an order of magnitude for the latter two species. Sedimentation might act to remove some of the condensed material from the stratosphere. Other chemicals, especially N_2O_5, ClO, and $ClNO_3$, may react on the surfaces of particles transforming the chemistry of the polar stratosphere in a manner that may be significant for the formation of the ozone hole.

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