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## HETEROGENEOUS PHYSICO-CHEMISTRY OF THE WINTER POLAR STRATOSPHERE

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Present chemical theories of the antarctic ozone hole assume that heterogeneous reactions involving polar stratospheric clouds (PSC's) are the precursor of springtime ozone depletions. However, none of the theories quantify the rates of proposed heterogeneous processes, and none utilize the extensive data base on PSC's. Thus, all of the theories must be considered incomplete until the heterogeneous mechanisms are properly defined. This paper develops a unified treatment of the cloud related processes, both physical and chemical, and calibrates the importance of these processes using observational data. We also compare the rates of competitive heterogeneous processes to place reasonable limits on critical mechanisms such as the denitrification and dechlorination of the polar winter stratosphere. Among the subjects addressed here are the physical/chemical properties of PSC's, including their relevant microphysical, optical and compositional characteristics, mass transfer rates of gaseous constituents to cloud particles, adsorption, accommodation and sticking coefficients on cloud particles, time constants for condensation, absorption and other microphysical processes, effects of solubility and vapor pressure on cloud composition, the statistics of cloud processing of chemically-active condensible species, rate-limiting steps in heterogeneous chemical reactions, and the nonlinear dependence of ozone loss on physical and chemical parameters.

For purposes of analysis, we distinguish two distinct types of PSC's, which we refer to as Type-I and Type-II PSC's. These cloud types have distinct properties that lead

to different rates for specific mechanical and chemical processes (see Table 1). Such distinctions have been neglected in previous theoretical models of the ozone hole. The Type-I PSC's are apparently composed of nitric acid ices. The thermodynamics and physical chemistry of such ices suggests that the nitric acid trihydrate may be the predominant form, although laboratory spectroscopic evidence also points to the formation of impure and amorphous ice structures under conditions similar to those found in the polar winter stratosphere. Type-II clouds are most likely composed primarily of water ice. The Type-II clouds have a substantially larger particle mass than Type-I PSC's, and are probably responsible for the observed dehydration and denitrification of the polar winter stratosphere in the region of the ozone hole. Type-I clouds, on the other hand, may be dominant in catalyzing heterogeneous reactions that lead to the observed repartition of HCl, ClONO<sub>2</sub>, and ClO. The frequency of occurrence of Type-I PSC's is roughly an order of magnitude greater than that of Type-II PSC's. Type-I clouds also fill a greater volume of the polar vortex over the course of winter.

The time constant for HCl absorption into ice particles is several hours or more in PSC's of either type. Although Type-I clouds may have only about 1% of the mass of Type-II clouds, they still have 10% or more of the surface area. The mass transfer rates of HCl to Type-I and II clouds occurs in different dynamical regimes: in Type-I clouds the HCl molecules reach ice surfaces by gas-kinetic transport; in Type-II clouds the HCl molecules diffuse toward particle surfaces in the transition flow regime lying between purely gas-kinetic and purely continuum flow. Gas-kinetic transport provides the more efficient mass transfer mechanism.

The removal of stratospheric trace gases condensed on PSC particles (e.g., HNO<sub>3</sub>, H<sub>2</sub>O and HCl) depends on the vapor

pressures of the condensates, the masses of condensates, the fallspeed of the particles, and the frequency and duration of cloud formation. The Type-I PSC ice particles have a gravitational fall velocity that is too low to account for the removal of substantial quantities of trace materials on short time scales (i.e., days to weeks). Nevertheless, the continuous sedimentation of these clouds over the course of winter can transfer materials downward by several kilometers on average. The measured particle sizes in Type-II clouds, by contrast, are large enough to carry condensed materials downward by several kilometers on time scales of hours to days.

The concentrations of trace constituents absorbed in ice particles also differs between the cloud types. In Type-I clouds, the HCl concentration could be ~1% by mass and the HNO<sub>3</sub> concentration ~50% by mass, while in Type-II clouds both the HCl and HNO<sub>3</sub> concentrations would be expected to lie below ~0.1% by mass. Such differences in concentrations are important in determining the rates of the heterogeneous chemical processes that involve chlorine species. For example, the short residence times and relatively low HCl concentrations of Type-II cloud particles implies that the reaction of ClONO<sub>2</sub> with condensed HCl might not proceed to completion in Type-II clouds. The competition between the processes of HCl condensation, HCl removal by cloud particle sedimentation, and HCl reaction with in situ ClONO<sub>2</sub> is thus sensitively dependent on the evolution of the Type-II PSC's and the dependence of the ClONO<sub>2</sub>/HCl reaction rate on the trace composition of the ice. The estimated time constants for a number of heterogeneous chemical processes are compared in Table 1.

A number of other topics will be discussed, including the relationship between the time constants for heterogeneous processes and the long-term evolution of the ozone hole.

TABLE 1. POLAR STRATOSPHERIC CLOUD PROPERTIES AND TIME CONSTANTS

Property	Type-I	Type-II	Type-III <sup>1</sup>
Composition	HNO <sub>3</sub> /3H <sub>2</sub> O	H <sub>2</sub> O+Trace <sup>2</sup>	H <sub>2</sub> O+Trace <sup>2</sup>
Mass	~1 ppbm	≤1 ppmm	~1 ppmm
Surface <sup>3</sup> Area	~10 <sup>-8</sup> cm <sup>2</sup> /cm <sup>3</sup>	~10 <sup>-7</sup> cm <sup>2</sup> /cm <sup>3</sup>	~10 <sup>-5</sup> cm <sup>2</sup> /cm <sup>3</sup>
Temperature Threshold <sup>4</sup>	~195 K	~187 K	~187 K
Relative Frequency <sup>5</sup>	~90%	~10%	~1%
Particle Diameter	~1 μm	~10-100 μm	~5 μm
Genesis Time <sup>6</sup>	~10 <sup>5</sup> sec	~10 <sup>3</sup> -10 <sup>4</sup> sec	~10 <sup>3</sup> sec
Cloud Particle Lifetime <sup>7</sup>	~10 <sup>5</sup> -10 <sup>6</sup> sec	<10 <sup>5</sup> sec	~10 <sup>3</sup> sec
Time to Fall 1 km	~1x10 <sup>7</sup> sec	~3x10 <sup>3</sup> -3x10 <sup>5</sup> sec	~1x10 <sup>6</sup> sec
HCl Absorption <sup>8</sup> Time	~1x10 <sup>5</sup> sec	~1x10 <sup>5</sup> sec	~10 <sup>2</sup> -10 <sup>3</sup> sec
HCl Concentration <sup>9</sup>	~0.01 g/g	~0.001 g/g	~0.001 g/g
ClONO <sub>2</sub> + HCl <sup>10</sup>	~1x10 <sup>5</sup> sec	~2x10 <sup>5</sup> sec	~10 <sup>3</sup> sec
ClONO <sub>2</sub> + H <sub>2</sub> O <sup>11</sup>	~1x10 <sup>6</sup> sec	~2x10 <sup>5</sup> sec	~10 <sup>3</sup> sec
N <sub>2</sub> O <sub>5</sub> + H <sub>2</sub> O <sup>12</sup>	~2x10 <sup>6</sup> sec	~4x10 <sup>5</sup> sec	~10 <sup>3</sup> sec
N <sub>2</sub> O <sub>5</sub> + HCl <sup>13</sup>	~2x10 <sup>6</sup> sec	~4x10 <sup>5</sup> sec	~10 <sup>3</sup> sec

## Footnotes

1. These are lee wave clouds, similar in character to Type-II PSC's, which are formed near orographic features. The Type-III clouds may be considered as a subset of the Type-II clouds with shorter lifetimes and stronger geographical localization.
2. The ice will contain traces of a number of soluble gases such as HCl, HNO<sub>3</sub>, HF and H<sub>2</sub>SO<sub>4</sub>, and the ice surfaces will hold many adsorbed vapors such as H<sub>2</sub>O, ClONO<sub>2</sub>, N<sub>2</sub>O<sub>5</sub> and HOCl.
3. Total particle surface area per unit volume of air.
4. The temperature threshold corresponds to the local frost point of water for Type-II and III clouds, which varies with the ambient pressure for a fixed water vapor mixing ratio.
5. Based on a preliminary statistical analysis of SAM II satellite measurements of PSC extinction during hundreds of sunrise and sunset events. A fraction of the Type-I clouds may be denser, but localized, Type-II and III clouds.
6. The formation time of Type-II clouds depends sensitively on the local water vapor supersaturation and its variation with time. The values shown roughly correspond to an average supersaturation of ~1%.
7. For Type-I clouds, the lifetime is limited by dynamical (cooling) processes, for Type-II clouds, by particle fallout, and for Type-III clouds, by dynamical (lee wave) processing.
8. Assuming the HCl is absorbed into pre-existing ice particles with a "sticking coefficient", or accommodation coefficient, of 0.4 (Leu, 1988). If the HCl co-condenses with the clouds, then the absorption time is similar to the "Genesis Time" given above.
9. The HCl concentration in Type-I cloud particles is estimated using vapor pressures over solid solutions of HCl in pure water ice as determined in recent laboratory studies (Molina et al., 1987). The vapor pressures of HCl over concentrated nitric acid ices are unknown, but are expected to be similar to those for pure water ice. The concentration of HCl in Type-II and III clouds is estimated assuming nearly complete absorption of ambient HCl vapor to form solid solutions in the ice, which is consistent with the measured solubility of HCl in ice (Molina et al., 1987).
10. Reaction time of ClONO<sub>2</sub> for the HCl concentrations given in this table and a ClONO<sub>2</sub> "sticking coefficient" (or reaction efficiency per collision, in this case) of 0.25 for Type-I clouds (Leu, 1988) and 0.02 for Type-II clouds; the latter value is an extrapolation to low HCl concentrations based on data from Leu (1988), Molina et al., 1987) and Tolbert et al., 1987). The estimated reaction times do not take into account competitive chemical and physical processes, and assumes ideal and uniform surface properties.
11. Assuming a ClONO<sub>2</sub> "sticking coefficient" of 0.02 for for pure ice (Type-II and III clouds) as well as nitric acid trihydrate ice (Type-I clouds) in the presence of excess environmental (condensed) water vapor. Measured values of the sticking coefficient on pure ice range from ~0.009 @ 185 K (Tolbert et al., 1987), to ~0.02 @ 200 K (Molina et al., 1987), to ~0.06 @ 200 K (Leu, 1988).
12. Assuming an N<sub>2</sub>O<sub>5</sub> "sticking coefficient" of 0.01 for ice surfaces in the presence of excess environmental water vapor; this value may represent a lower limit for the reaction on pure ice at temperatures of ~190-200 K (M.-T. Leu, prvt. comm., 1988).
13. Adopting an estimated N<sub>2</sub>O<sub>5</sub> "sticking coefficient" of 0.01 for all types of PSC cloud surfaces and HCl concentrations (see Footnotes 11 and 12).