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Condensational Growth and Trace Species Scavenging in Stratospheric Sulfuric Acid/Water Aerosol Droplets

by

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The Earth's atmosphere can generally be divided into two parts, the troposphere at lower levels and the stratosphere at higher levels. These two levels are separated by the tropopause and generally have very different properties. The height of the tropopause depends upon the latitude and varies from about 9 km at 60°N/S to about 13 km at 20°N/S.

Stratospheric aerosols were discovered about 1961 [Junge et al.] and have since been recognized to play a significant role in the environment. The composition of stratospheric aerosol is believed to be a liquid solution of sulfuric acid (H_2SO_4) and water (H_2O) with numerous trace species [Rosen; Hamill et al.]. Of these trace species, ozone (O_3) in particular has been recognized as being very important in its role of shielding the environment from harmful ultraviolet radiation. Also among the trace species are HCl and $ClONO_2$, the so called 'chlorine reservoir' species and various oxides of nitrogen such as NO, NO_2, and N_2O_5.

The quantity of stratospheric aerosol and its particle size distribution determines, to a large degree, the chemistry present in the stratosphere. $ClONO_2$ and HCl react with water and N_2O_5 on droplet surfaces to produce the ozone reactive species HOCl, Cl_2, and $ClNO_2$ (eqn. 1) which subsequently destroy the ozone [Watson et al.]. A principal product of these reactions is nitric acid (HNO_3) which is generally lost through absorption by the aerosol droplets. This results in a 'denitrification' of the stratosphere [Van Doren et al.]. Loss of these nitrogen compounds suppresses the reformation of the chlorine reservoir species and thus enhances ozone depletion. The NO and NO_2 species play a role in both ozone production and removal but have their own removal mechanisms involving the formation of HNO_3 [Mozurkewich and Calvert]. This removal represents a further denitrification of the stratosphere.

Aerosols experience three types of growth: nucleation, condensation, and coagulation. The term 'growth' in this context also encompasses the corresponding size decreasing mechanisms of disintegration, evaporation, and fragmentation. Nucleation and condensation have probably been studied the most extensively. In particular, extensive work has been done on the nucleation of stratospheric sulfuric acid/water droplets [e.g. Yue; Singh et al.]. Much generic work has been done on the problem of condensation [e.g. Tompson and Loyalka; Loyalka et al.]. The current effort seeks to apply the latter work [Loyalka et al.] to the specific problem of stratospheric aerosols.

The transport of various trace gas species to and from a droplet can be thought of as condensation and evaporation. The ultimate driving term for each species' condensation is the gradient of its density at the surface of the droplet or, more simply, the difference between its bulk background density and its saturation density at the droplet surface. Many things can modify these density gradients and each factor would have to be considered in a comprehensive model. For the present we simply consider these densities to be known.

The previous results that are followed [Loyalka et al.] are the numerically calculated condensation rates for a vapor species diffusing through some noncondensing background gas. Where the vapor is incident on a spherical droplet it is assumed to condense and to reach thermal equilibrium with the droplet. The vapor is assumed to have a much lower density than the background gas such that the velocity distribution function for the vapor is determined by a linear form of the transport equation (Boltzmann's equation; eqn. 2) with appropriate boundary conditions (eqn. 3). The boundary conditions are interpreted to mean that all of the incident vapor molecules reach thermal equilibrium as stated previously and that far from the droplet the usual continuum theory (Diffusion theory) applies. Discretization of the above problem leads to an expression for the condensation rate (eqn. 4) and a series of appropriate iterative formulas (eqn. 5). Table 1 lists the results of this previous work in a convenient dimensionless form. As can be seen, these results are generic in that they do not apply to any specific combination of gases.

In this work, the previous results have been employed to obtain values of the condensation rates for specific trace species in the stratosphere. The values thus determined assume a background gas of N_2 and are listed in Table 2. Work is currently underway to integrate these values into a reasonably comprehensive, dynamic model of stratospheric droplet behavior. The droplet sizes in the above results have been expressed in units of the molecular mean free path.

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$$
\begin{aligned}
\mathrm{ClONO_2 + H_2O(aq)} &\rightarrow \mathrm{HOCl + HNO_3(aq)} \\
\mathrm{ClONO_2 + HCl(aq)} &\rightarrow \mathrm{Cl_2 + HNO_3(aq)} \\
\mathrm{N_2O_5 + HCl(aq)} &\rightarrow \mathrm{ClNO_2 + HNO_3(aq)} \\
\mathrm{N_2O_5 + H_2O(aq)} &\rightarrow \mathrm{2\ HNO_3(aq)}
\end{aligned}
\tag{1}
$$

$$
\mathbf{c} \cdot \frac{\partial h_m}{\partial \mathbf{r}} = \hat{L} h_m \tag{2}
$$

$$
h_m(R, c, \mu) = 0, \quad \mu > 0
$$

$$
\lim_{r \to \infty} h_m(r, c, \mu) = \left(\frac{n_{\mathrm{asy}}(r) - n_s}{n_s} \right) + \mathbf{c} \phi_d(c) \cdot \frac{1}{n_s} \frac{d}{d\mathbf{r}} n_{\mathrm{asy}}(r) = \left(\frac{n_\infty - n_s}{n_s} \right) + \hat{u}(r) \frac{1}{r} \left(-1 + \frac{\mathbf{c} \cdot \mathbf{n}_r}{r} \phi_d(c) \right) \tag{3}
$$

$$
\hat{u}(R) = \left(\frac{n_\infty - n_s}{n_s} \right) \left(\frac{\sqrt{\pi}}{R^2} - 4\pi^{3/2} \sum_{j=1}^{J} c_j^2 w_j \sum_{m=2,4,\dots}^{N} \omega_m \mu_m \psi_{mj}^{1/2} \right)^{-1} \tag{4}
$$

for $\mu_m = -1$,

$$
\bar{\psi}_{-1j}^{i+1/2} = \frac{(A_{i+1} + A_i)\psi_{-1j}^{i+1} + V_{i+1/2} q_{-1j}^{i+1/2}}{(A_{i+1} + A_i) + V_{i+1/2} \sigma_j}
$$

for $-1 < \mu_m < 0$,

$$
\bar{\psi}_{mj}^{i+1/2} = \frac{-\mu_m (A_{i+1} + A_i)\psi_{mj}^{i-1} + (1/\omega_m)(a_{m+1j}^{i+1/2} + a_{m-1j}^{i+1/2})\psi_{m-1j}^{i+1/2} + V_{i+1/2} q_{mj}^{i+1/2}}{-\mu_m (A_{i+1} + A_i) + (1/\omega_m)(a_{m+1j}^{i+1/2} + a_{m-1j}^{i+1/2}) + V_{i+1/2}\sigma_j} \tag{5a}
$$

for $\mu_m > 0$,

$$
\bar{\psi}_{mj}^{i+1/2} = \frac{\mu_m (A_{i+1} + A_i)\psi_{mj}^{i-1} + (1/\omega_m)(a_{m+1j}^{i+1/2} + a_{m-1j}^{i+1/2})\psi_{m-1j}^{i+1/2} + V_{i+1/2} q_{mj}^{i+1/2}}{\mu_m (A_{i+1} + A_i) + (1/\omega_m)(a_{m+1j}^{i+1/2} + a_{m-1j}^{i+1/2}) + V_{i+1/2}\sigma_j}
$$

$$\psi^{i}_{mj} = 2\bar{\psi}^{i+1/2}_{mj} - \psi^{i+1}_{mj}$$

$$\psi^{i+1/2}_{m+1\,j} = 2\bar{\psi}^{i+1/2}_{mj} - \psi^{i+1/2}_{m-1\,j}$$

$$\sigma_j = \sigma(\beta c_j)$$

$$A_i = 4\pi r_i^2$$

$$V_{i+1/2} = (4\pi/3)(r_{i+1}^3 - r_i^3)$$

$$a^{i+1/2}_{1j} = a^{i+1/2}_{2N+1\,j} = 0$$

$$a^{i+1/2}_{m+1\,j} = a^{i+1/2}_{m-1\,j} - \omega_m \mu_m (A_{i+1} - A_i)$$

(5b)

$$q^{i}_{mj} = \epsilon \exp(-c_j^2) \sum_{l=0}^{L} \frac{2l+1}{2} P_l(\mu_m)$$

$$\times \sum_{j'=1}^{J} c_{j'} w_{j'} k_l(c_j, c_{j'}) \sum_{m'=2,4,\ldots}^{2N} \omega_{m'} \psi^{il}_{m'j'} ,$$

$$\psi^{il}_{mj} = P_l(\mu_m)\tfrac{1}{2}(\psi^{i-1/2}_{mj} + \psi^{i+1/2}_{mj})$$

$$\psi^{i}_{mj} \triangleq \psi^{i0}_{mj} .$$

Table 1: The dimensionless condensation rate from [Loyalka et al.].

R	β^2=0.1	β^2=0.5	β^2=1.0	β^2=10.0
0.1	0.9884	0.9782	0.9770	0.9734
0.25	0.9490	0.9415	0.9401	0.9342
0.5	0.8765	0.8706	0.8688	0.8612
0.75	0.8060	0.8012	0.7990	0.7908
1.0	0.7410	0.7374	0.7353	0.7273
1.25	0.6824	0.6802	0.6783	0.6710
1.5	0.6304	0.6293	0.6279	0.6215
1.75	0.5845	0.5842	0.5832	0.5779
2.0	0.5440	0.5443	0.5436	0.5392
3.0	0.4224	0.4223	0.4226	0.4214
5.0	0.2885	0.2887	0.2891	0.2894
10.0	0.1594	0.1594	0.1595	0.1598
20.0	0.0834	0.0834	0.0835	0.0836
50.0	0.0342	0.0342	0.0343	0.0343
100.0	0.0172	0.0172	0.0172	0.0173

Table 2a: The dimensionless condensation rates for stratospheric vapor species.

R	H_2O	H_2SO_4	SO_2	HCl
0.01	0.9967	0.9974	0.9975	0.9963
0.02	0.9945	0.9959	0.9956	0.9941
0.05	0.9876	0.9911	0.9896	0.9874
0.07	0.9829	0.9878	0.9855	0.9829
0.1	0.9758	0.9826	0.9793	0.9760
0.2	0.9514	0.9577	0.9550	0.9520
0.5	0.8670	0.8733	0.8713	0.8689
0.7	0.8110	0.8172	0.8155	0.8131
1.0	0.7332	0.7391	0.7378	0.7359
1.2	0.6871	0.6922	0.6914	0.6897
1.5	0.6265	0.6299	0.6295	0.6286
1.7	0.5903	0.5930	0.5928	0.5922
2.0	0.5429	0.5442	0.5443	0.5441
3.0	0.4229	0.4223	0.4223	0.4224
5.0	0.2895	0.2886	0.2887	0.2889
7.0	0.2027	0.2018	0.2019	0.2020
10.0	0.1596	0.1594	0.1594	0.1594
20.0	0.0836	0.0834	0.0834	0.0834
50.0	0.0344	0.0342	0.0342	0.0342
70.0	0.0178	0.0176	0.0176	0.0177
100.0	0.0173	0.0172	0.0172	0.0172

Table 2b: The dimensionless condensation rates for stratospheric vapor species.

R	HOCl	Cl_2	$ClNO_2$	$ClONO_2$
0.01	0.9975	0.9974	0.9973	0.9974
0.02	0.9954	0.9956	0.9956	0.9959
0.05	0.9889	0.9899	0.9904	0.9911
0.07	0.9845	0.9860	0.9868	0.9877
0.1	0.9777	0.9801	0.9812	0.9826
0.2	0.9538	0.9557	0.9566	0.9577
0.5	0.8703	0.8718	0.8724	0.8732
0.7	0.8146	0.8159	0.8164	0.8171
1.0	0.7372	0.7382	0.7386	0.7391
1.2	0.6909	0.6916	0.6919	0.6922
1.5	0.6292	0.6296	0.6297	0.6299
1.7	0.5927	0.5929	0.5929	0.5930
2.0	0.5443	0.5443	0.5443	0.5442
3.0	0.4223	0.4223	0.4223	0.4223
5.0	0.2887	0.2886	0.2886	0.2886
7.0	0.2019	0.2018	0.2018	0.2018
10.0	0.1594	0.1594	0.1594	0.1594
20.0	0.0834	0.0834	0.0834	0.0834
50.0	0.0342	0.0342	0.0342	0.0342
70.0	0.0177	0.0176	0.0176	0.0176
100.0	0.0172	0.0172	0.0172	0.0172

Table 2c: The dimensionless condensation rates for stratospheric vapor species.

R	HNO_3	NO	NO_2	N_2O_5
0.01	0.9976	0.9971	0.9968	0.9975
0.02	0.9956	0.9949	0.9947	0.9961
0.05	0.9896	0.9881	0.9881	0.9915
0.07	0.9855	0.9835	0.9837	0.9883
0.1	0.9791	0.9764	0.9768	0.9834
0.2	0.9549	0.9524	0.9529	0.9583
0.5	0.8712	0.8687	0.8697	0.8737
0.7	0.8154	0.8128	0.8140	0.8175
1.0	0.7378	0.7354	0.7367	0.7394
1.2	0.6914	0.6893	0.6905	0.6924
1.5	0.6295	0.6281	0.6290	0.6300
1.7	0.5928	0.5918	0.5925	0.5930
2.0	0.5443	0.5438	0.5442	0.5442
3.0	0.4223	0.4225	0.4223	0.4223
5.0	0.2887	0.2890	0.2888	0.2886
7.0	0.2019	0.2021	0.2019	0.2018
10.0	0.1594	0.1595	0.1594	0.1594
20.0	0.0834	0.0835	0.0834	0.0834
50.0	0.0342	0.0343	0.0342	0.0342
70.0	0.0176	0.0177	0.0177	0.0176
100.0	0.0172	0.0172	0.0172	0.0172

All values of the dimensionless condensation rate can be multiplied by the appropriate value of the free molecular condensation rate from the below equation to obtain the actual, dimensionally correct condensation rate for any specific system of interest:

$$\tilde{u}_{fm}(\tilde{R}) = \pi \tilde{R}^2 \rho_0 \left(\frac{8\,k\,T}{\pi\, m} \right)^{1/2} \left(\frac{n_\infty - n_s}{n_s} \right)$$

where:

$\tilde{u}_{fm}(\tilde{R})$ is the free molecular condensation rate
$\tilde{R}$ is the droplet radius
ρ_0 is the vapor saturation mass density
k is Boltzmann's constant
T is the system temperature
m is the mass of a vapor molecule
n_∞ is the bulk number density of the vapor
n_s is the saturation number density of the vapor