A model for studying the composition and chemical effects of stratospheric aerosols

Azadeh Tabazadeh, Richard P. Turco and Mark Z. Jacobson
Department of Atmospheric Sciences, University of California, Los Angeles

Abstract. We developed polynomial expressions for the temperature dependence of the mean binary and water activity coefficients for \( \text{H}_2\text{SO}_4 \) and \( \text{HNO}_3 \) solutions. These activities were used in an equilibrium model to predict the composition of stratospheric aerosols under a wide range of environmental conditions. For typical concentrations of \( \text{H}_2\text{O}, \text{H}_2\text{SO}_4, \text{HNO}_3, \text{HCl}, \text{HBr}, \text{HF}, \text{and HOCI} \) in the lower stratosphere, the aerosol composition is estimated as a function of the local temperature and the ambient relative humidity. For temperatures below 200 K, our results indicate that (1) \( \text{HNO}_3 \) contributes a significant mass fraction to stratospheric aerosols, and (2) \( \text{HCl} \) solubility is considerably affected by \( \text{HNO}_3 \) dissolution into sulfate aerosols. We also show that, in volcanically disturbed periods, changes in stratospheric aerosol composition can significantly alter the microphysics that leads to the formation of polar stratospheric clouds. The effects caused by \( \text{HNO}_3 \) dissolution on the physical and chemical properties of stratospheric aerosols are discussed.

Introduction

Heterogeneous processes on the surfaces of polar stratospheric clouds (PSCs) play a key role in the formation of the ozone hole in the Antarctic [Solomon et al., 1986; Turco et al., 1989]. Moreover, during the past few years, laboratory and modeling studies have shown that heterogeneous reactions on naturally occurring sulfuric acid aerosols may impact ozone on a global scale [Tolbert et al., 1988; Hofmann and Solomon, 1989; Hanson and Ravishankara, 1991; Turco and Hamill, 1992; Granier and Brasseur, 1992; Prather, 1992]. Following major volcanic eruptions, stratospheric sulfuric acid injection by volcanos can enhance the abundance of sulfate aerosols, creating a source of large-scale ozone depletion. Dissolution and reactions of \( \text{HCl} \) and other species in volcanic aerosols are crucial to the ozone problem. To address such issues, we have developed a new equilibrium model to calculate solubilities of various species in stratospheric aerosols as a function of local temperature, relative humidity, and the trace composition of the surrounding air.

Considerable amount of laboratory work has been done to measure the solubility of \( \text{HCl} \) and \( \text{HNO}_3 \) in sulfuric acid solutions. Solubilities are often expressed in terms of an effective Henry's constant (\( \text{H'} \)). \( \text{H'} \) is defined as the ratio of the dissolved species in solution to the equilibrium partial pressure of the species over the solution. The laboratory measurements of \( \text{H'} \) are either kinetic [Reihl et al., 1990; Watson et al., 1990; Van Doren et al., 1991; Williams and Golden, 1993; Hanson and Ravishankara, 1993] or equilibrium in nature [Zhang et al., 1993a]. In the kinetic experiments, \( \text{H'} \) is calculated indirectly from the measurements of time-dependent uptake coefficient, which varies as a function of the gas accommodation coefficient and liquid-phase diffusion coefficient. Measuring or estimating these coefficients can introduce errors in the extracted value of \( \text{H'} \). However, in the equilibrium method, \( \text{H'} \) is calculated directly from equilibrium vapor pressure measurements over a known solution composition. We have used data obtained from the latter technique to validate the solubilities predicted by our model. Jaecker-Voirol et al. [1990] and Luo et al. [1994] have modeled the solubility of \( \text{HNO}_3 \) and \( \text{HCl} \), respectively, in sulfuric acid solutions using \( \text{HNO}_3 \) and \( \text{HCl} \) activity coefficients. The activities were extrapolated from laboratory measurements at room temperatures. Here we used recent laboratory measurements [Zhang et al., 1993a, b], along with tables for apparent enthalpy, heat capacity, and activity coefficients to extrapolate room temperature binary activities (solute and solvent) to stratospheric temperatures. We then use these binary activities in a new equilibrium solver (M. Z. Jacobson et al., Simulating equilibrium within aerosols and non-equilibrium between gases and aerosols, submitted to Journal of Geophysical Research, 1994) to predict solubilities for various species in \( \text{H}_2\text{SO}_4/\text{H}_2\text{O} \) and \( \text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O} \) solutions. In sum, we found that, at higher temperatures (> 210 K), stratospheric aerosols are mainly \( \text{H}_2\text{SO}_4/\text{H}_2\text{O} \) solutions. For \( T < 200 \text{ K} \), \( \text{HNO}_3 \) is a major component of these aerosols, and its aqueous concentration increases rapidly as temperature decreases. If aerosols remain supercooled, then ternary solutions of \( \text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O} \) eventually convert to \( \text{HNO}_3/\text{H}_2\text{O} \) solutions. We also show that, if volcanic clouds are present when temperatures are < 200 K, then the major \( \text{HNO}_3 \)-containing aerosols are composed of ternary solutions of \( \text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O} \) instead of nitric acid trihydrate (NAT) particles. The impact of \( \text{HNO}_3 \) dissolution on the solubility and reactivity of \( \text{HCl} \) in the stratospheric aerosols are discussed.

2. Binary Strong Electrolyte Systems

To describe the equilibrium of strong electrolyte univalent acids in water, we adopted the Brimblecombe and Clegg [1988] activity formulation. This model is applied to the
HNO₃, HCl and HBr binary solutions in water. In the case of H₂SO₄, we used recent laboratory measurements on the properties of H₂SO₄/H₂O solutions to derive new deliquescence curves and activity coefficients for this system [Zhang et al., 1993a, b].

2.1. Univalent Electrolyte Systems

Brimblecombe and Clegg [1988] have shown that, for strong electrolytes in water solutions, the solubility is best described by an equilibrium between the gas phase and the respective ions in solution, given by

\[ HA(g) \leftrightarrow H^+(aq) + A^-(aq) \] (1)

Once the mean activity coefficient is determined at the standard temperature, its value at other temperatures can be calculated using temperature extrapolations [Clegg and Brimblecombe, 1990]

\[ \log \gamma_+ (T) = \log \gamma_+ (T^o) + \frac{1}{v} (yL_2 - J_2 + \Omega_2) \] (6a)

\[ y = (T^o - T) / (2.303RT^oT) \] (6b)

\[ z = T^o y - \log (T^o / T) / R \] (6c)

\[ \Omega = T^o (z + 1/2(T - T^o)) \] (6d)

where \( L_2 \) (calorie/mole) and \( J_2 \) (calorie/mole-Kelvin) are the partial molal enthalpy and heat capacity of the solute, respectively, \( v \) is the number of ions produced by the complete dissociation of one molecule of solute. The term \( \Omega_2 \) is equal to \( \partial J_2 / \partial T \) evaluated at the standard temperature and concentration of interest. The partial molal quantities (\( \gamma \) and \( J \)) are related to the apparent molal quantities (\( \gamma \) and \( J \)) by [Clegg and Brimblecombe, 1990]

\[ L_2 = \gamma L + m(\partial \gamma / \partial m) \] (7a)

\[ J_2 = \gamma J + m(\partial J / \partial m) \] (7b)

Thus for a known equilibrium composition (\( S \)), the equilibrium vapor pressure over the solution (\( P_{HA} \)) is equal to \( S^2 \gamma^2_+ / K_2 \). The overall gas solubility constant (\( K_2 \)) varies with temperature and the overall gas solubility constant (\( K_2 \)) at the standard temperature (\( T^o \)) is approximated using the van't Hoff equation

\[ \ln \left( \frac{K_2}{K_{2o}} \right) = \frac{\Delta H^o}{R} \left( \frac{1}{T^o} - \frac{1}{T} \right) + \frac{\Delta C^o_p}{R} \left( T^o - T - \ln \left( T^o / T \right) \right) \] (4)

where \( \Delta H^o \) (calorie/mole) and \( \Delta C^o_p \) (calorie/Kelvin-mole) are the enthalpy and the heat capacity changes, respectively, for the process described in (1) at the standard temperature (\( T^o = 298.15 \) K). Table 1 lists the appropriate parameters for the electrolyte solutions studied in this work. \( K_{2o} \) and \( K_{2i} \) are the overall gas solubility constants at temperatures \( T^o \) and \( T^i \), respectively.

The mean activity coefficient, \( \gamma_+ \), in equation (2) can be calculated for a given molality at the standard temperature (\( T^o \)) from [Hammer and Wu, 1972]

\[ \log \gamma_+ (T^o) = -0.5108m^{1/2} + \frac{\beta m + C m^2 + D m^3 + Em^4 + F m^5}{1 + B m^{1/2}} \] (5)

where the parameters \( B, \beta, C, D, E \) and \( F \) are determined experimentally for each electrolyte HA [Hammer and Wu, 1972], and \( m \) is the molality of HA in solution. These parameters are given in Table 2 for several electrolytes studied here.

---

Table 1. Thermodynamic Parameters

<table>
<thead>
<tr>
<th>Species</th>
<th>( K_s ), mol²/kg² atm</th>
<th>( \Delta C^o_p ), cal/K mol</th>
<th>( \Delta H^o ), kcal mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>2.45e+6</td>
<td>-3.34704e+1</td>
<td>-1.74713e+1</td>
</tr>
<tr>
<td>HCl</td>
<td>2.04e+6</td>
<td>-3.95793e+1</td>
<td>-1.78967e+1</td>
</tr>
<tr>
<td>HBr</td>
<td>1.32e+9</td>
<td>-9.76820e+0</td>
<td>-2.03537e+1</td>
</tr>
</tbody>
</table>

Parameters were taken from Brimblecombe and Clegg [1988]. Read 2.45e+6 as 2.45x10⁶.
Table 2. Activity Parameters

<table>
<thead>
<tr>
<th>Species</th>
<th>Molality Range</th>
<th>B'</th>
<th>β</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>0-28</td>
<td>1.5824</td>
<td>6.2432e-2</td>
<td>-1.3137e-3</td>
<td>-1.2886e-5</td>
<td>4.917e-7</td>
<td>0.0</td>
</tr>
<tr>
<td>HCl</td>
<td>0-16</td>
<td>1.5250</td>
<td>1.0494e-1</td>
<td>6.5360e-3</td>
<td>-4.2058e-4</td>
<td>-4.070e-6</td>
<td>5.258e-7</td>
</tr>
<tr>
<td>HBr</td>
<td>0-10</td>
<td>1.6468</td>
<td>1.2457e-1</td>
<td>8.8530e-3</td>
<td>2.4750e-5</td>
<td>-3.719e-5</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Parameters were taken from Hammer and Wu (1972). Read 6.2432e-2 as $6.2432 \times 10^{-2}$.

(5). The integrated form of equation (8b) is given by Hammer and Wu [1972]. The water activity at other temperatures is related to the water partial molal enthalpy ($L_a$), and heat capacity ($J_t$) by [Clegg and Brimblecombe, 1992]

$$\log a_w(T) = \log a_w(T_0) + yL_t - zJ_t + \Omega$$

where the term $\Omega$ is equal to $\partial L_t / \partial T$ evaluated at the standard temperature and concentration of interest, and the partial water molal quantities are related to the apparent molal quantities ($L_t$ and $C_{p_t}$) by [Clegg and Brimblecombe, 1990]

$$L_t = -0.018m^2(\partial L_t / \partial m)$$

$$J_t = -0.018m^2(\partial C_{p_t} / \partial m)$$

For atmospheric applications, the water activity is equal to the ambient relative humidity, which is defined as the ratio of water vapor partial pressure to the water vapor saturation pressure. Thus, for a constant water vapor pressure profile, the temperature variation of water activity over a binary solution can be calculated if the saturation vapor pressure of water is known. For temperatures below 250 K, the saturation vapor pressure of water in units of torr is given as [Clegg and Brimblecombe, 1990]

$$p_{H_2O}^{sat} = \exp\{23.630958 - 5832.42478/T\} - (1.01358 \times 10^{-5})T^2$$

Solving equations (8) through (11) analytically for the pure electrolyte molality, the deliquescence curves can be computed for various binary solutions in water. The deliquescence curve describes the quantitative relationship between temperature and the equilibrium binary solution composition for a constant water vapor pressure profile.

In most binary equilibrium vapor pressure measurements, the aqueous electrolyte concentration is usually expressed either as weight percent or mole fraction. For application in the model described above, all the concentration units need to be converted to molalities. There are simple relations between molality, weight percent, and mole fraction, given by

$$m = \frac{1000W}{M(100-W)} = \frac{1000X}{18(1-X)}$$

where $W$ and $X$ are the weight percent and mole fraction of the electrolyte in solution, respectively, and $M$ is the electrolyte molecular weight in grams.

2.1.1. HNO₃/H₂O system. For this system, we compared model predictions of the HNO₃ and H₂O vapor pressures over nitric acid solutions to the low-temperature measurements of Hanson and Mauersberger [1988a] and Hanson [1990]. We used (2) through (7) to calculate the vapor pressure of HNO₃ over HNO₃/H₂O solutions for a known composition (5). For computations, the $\Gamma_2$ function for HNO₃/H₂O system is given by [Clegg and Brimblecombe, 1990]

$$\Gamma_2 = 0.4236x_1(x_1 - 2) - 0.08484x_1^2(5x_1 - 7)$$

where $x_1$, the mole fraction of all ions (H⁺ and NO₃⁻) in solution, is related to the HNO₃ molality ($m$) in solution by

$$x_1 = \frac{2m}{2m + 55.556}$$

Figure 1a shows the results of our calculations. The dashed lines are least squares fits for the vapor pressure of nitric acid over HNO₃/H₂O solutions, taken form Hanson and Mauersberger [1988a] and Hanson [1990]. Our results are in excellent agreement with respect to the HNO₃ vapor pressure over this binary solution. For simple application, we have fit

Table 3. Apparent Enthalpy

<table>
<thead>
<tr>
<th>Species</th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
<th>$a_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>5.7200068e+1</td>
<td>-5.4128777e+0</td>
<td>1.4870927e+1</td>
<td>-6.6184600e-1</td>
<td>1.20959091e-2</td>
<td>-8.0648265e-5</td>
</tr>
<tr>
<td>HCl</td>
<td>7.2685004e+1</td>
<td>2.2199006e+2</td>
<td>4.5003161e+0</td>
<td>-3.3699635e-1</td>
<td>8.44789761e-3</td>
<td>-7.197069e-5</td>
</tr>
<tr>
<td>HBr</td>
<td>2.2684938e+2</td>
<td>9.8258222e+1</td>
<td>1.2064140e+1</td>
<td>-3.4513187e-1</td>
<td>3.14050852e-3</td>
<td>-3.7356295e-6</td>
</tr>
</tbody>
</table>

Polynomials were fitted to Lide's [1990] data on the apparent enthalpy for solute molalities > 1. Read 5.7200068e-1 as $5.7200068 \times 10^{-1}$.
Polynomials were fitted to Lide's data [1990] on the apparent heat capacity for solute molalities > 1. Read 
-2.0103909e+1 as -2.0103909 x 10^1.

the model generated mean activity coefficient results into a polynomial function in HNO₃ molality (mₙ), given by

$$
\ln \gamma^*ₙ = \sum_{i=0}^{5} a_i(T) m_i^n
$$

where the $\gamma^*ₙ$ is the HNO₃ mean activity coefficient, and $a_i$ variables are temperature coefficients given in Table 5. Note that from now on equation (15) is used to calculate the mean activity coefficient for HNO₃ instead of equations (5) through (7).

To calculate the equilibrium H₂O vapor pressure, we solved the water activity equation for a known solution composition and temperature from (8). The equilibrium water vapor pressure over the binary system was obtained by multiplying the computed water activity by the water saturation vapor pressure from (11). For computations, the $\Gamma_i$ function for HNO₃/H₂O system was [Clegg and Brimblecombe, 1990]

$$
\Gamma_i = 0.2390 x_i^2 (0.8861 - 0.8774 x_i)^3
$$

Model results are compared to low-temperature measurements of Hanson and Mauersberger [1988a] and Hanson [1990] in Figure 1b. Our results are in good agreement with respect to the water vapor pressure over this binary solution. The deliquescence curves for the HNO₃/H₂O system were calculated from (8) for stratospheric temperatures and humidities. For simple application, we have fit the model-generated water activities into a polynomial function with respect to water vapor pressure ($P_w$) in units of torr, given by

$$
m_w^n = \sum_{i=0}^{5} (-1)^i N_i(T) P_w^i
$$

where $m_w^n$ is the molality for a pure HNO₃/H₂O system, and $N_i$ variables are temperature coefficients, given in Table 6.

In addition, we also solved (2), (15) and (17) simultaneously to calculate the condensation point ($T_c$) of HNO₃/H₂O solutions in the stratosphere, given by

$$
T_c = \frac{B(P_w)}{A(P_w)} - \ln P_{HNO₃}
$$

where $P_w$ and $P_{HNO₃}$ are ambient H₂O and HNO₃ vapor pressures in units of torr, and $A$ and $B$ are pressure coefficients given in Table 7. Figure 2 shows condensation points of aqueous HNO₃ solutions as a function of H₂O and HNO₃ vapor pressures. Note that under typical stratospheric conditions (P$_{H₂O}$ ~ 2 - 3 x 10⁻⁴ torr and P$_{HNO₃}$ ~ 2 - 8 x 10⁻⁷ torr), the condensation point of HNO₃/H₂O solutions are ~ 191 - 193 K (Figure 2). This is about 3 - 4 K lower than the nitric acid trihydrate frost point (~ 195 - 196 K), and is about 1 - 3 K higher than the ice frost point (~ 188 - 190 K) [Hanson, 1990].

### Table 4. Apparent Heat Capacity

<table>
<thead>
<tr>
<th>Species</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
<th>$b_4$</th>
<th>$b_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃</td>
<td>-2.0103909e+1</td>
<td>7.7423887e+0</td>
<td>-5.663838e+0</td>
<td>2.0842130e+0</td>
<td>-3.7501139e+0</td>
<td>2.6149276e-6</td>
</tr>
<tr>
<td>HCl</td>
<td>-3.1787735e+1</td>
<td>6.6553697e+0</td>
<td>-1.4355236e+0</td>
<td>1.8361194e+0</td>
<td>-1.1043527e-2</td>
<td>2.4811100e-4</td>
</tr>
<tr>
<td>HBr</td>
<td>-3.3252952e+1</td>
<td>5.6691907e+0</td>
<td>-7.9187247e-1</td>
<td>7.3203752e-2</td>
<td>-3.2890892e-3</td>
<td>5.4783763e-5</td>
</tr>
</tbody>
</table>

Polynomials were fitted to Lide's data [1990] on the apparent heat capacity for solute molalities > 1. Read -2.0103909e+1 as -2.0103909 x 10^1.
Table 5. Temperature Dependence for the Activity Parameters

\[ a_j = b_0 + b_1T + b_2T^2 + b_3T^3 + b_4T^4 \]

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>( b_0 )</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( b_3 )</th>
<th>( b_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{SO_2} )</td>
<td>-9.8727713620e+1</td>
<td>1.5892180900e+0</td>
<td>-1.06161069051e-2</td>
<td>3.1437317659e-5</td>
<td>-3.5694366687e-8</td>
</tr>
<tr>
<td>( a_{NO_2} )</td>
<td>2.6972534510e+1</td>
<td>-4.1774112495e-1</td>
<td>2.7534709328e-3</td>
<td>-9.805272503e-6</td>
<td>9.0199849894e-9</td>
</tr>
<tr>
<td>( a_{HNO_3} )</td>
<td>-3.1506575361e+0</td>
<td>5.1477027999e+0</td>
<td>-3.4974703589e-2</td>
<td>1.0511865215e-5</td>
<td>-1.2167638793e-9</td>
</tr>
<tr>
<td>( a_{HCl} )</td>
<td>8.9194643751e-2</td>
<td>-1.4398498843e-2</td>
<td>9.5874823381e-3</td>
<td>-2.8832908378e-6</td>
<td>3.3199717594e-11</td>
</tr>
</tbody>
</table>

2.1.2. HCl/H₂O system. For this system, we compare the model predictions of the HCl vapor pressure over HCl/H₂O solutions to the measurements of Fritz and Fuget [1956]. Using equations (2) through (7), we computed the HCl vapor pressure over solutions ranging from 1 to 37 % HCl by weight. To obtain the results below, we estimated \( \Gamma_2 \) from the extensive studies of Holmes et al. [1987] and Fritz and Fuget [1956] on the thermodynamic properties of the HCl/H₂O system, which is

\[ \ln N_1(T) = a_0 + a_1/T + a_2/T^2 + a_3/T^3 + a_4/T^4 \]

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>( a_0 )</th>
<th>( a_1 )</th>
<th>( a_2 )</th>
<th>( a_3 )</th>
<th>( a_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( N_0 )</td>
<td>2.5757237579e-1</td>
<td>3.4615149493e+3</td>
<td>-1.1460419802e+6</td>
<td>1.6003066569e+8</td>
<td>-8.2005020704e+9</td>
</tr>
<tr>
<td>( N_1 )</td>
<td>-2.3081801501e+1</td>
<td>9.7545732474e+3</td>
<td>-1.0751476647e+6</td>
<td>1.2845681641e+9</td>
<td>-5.638733805e+9</td>
</tr>
<tr>
<td>( N_2 )</td>
<td>-1.1454916074e+2</td>
<td>6.7577746435e+4</td>
<td>-1.5833469853e+7</td>
<td>2.0068038322e+9</td>
<td>-9.5789893230e+10</td>
</tr>
<tr>
<td>( N_3 )</td>
<td>-3.7614906611e+2</td>
<td>2.5721043666e+5</td>
<td>-6.9093891724e+7</td>
<td>8.8862582626e+9</td>
<td>-4.3013954256e+11</td>
</tr>
<tr>
<td>( N_4 )</td>
<td>-1.1566205559e+3</td>
<td>8.5657451707e+5</td>
<td>-2.4368087899e+8</td>
<td>3.1789555772e+10</td>
<td>-1.5566652191e+12</td>
</tr>
<tr>
<td>( N_5 )</td>
<td>-2.985872606e+3</td>
<td>2.2912842052e+6</td>
<td>-6.6825883931e+8</td>
<td>8.7835101682e+10</td>
<td>-4.330365673e+12</td>
</tr>
</tbody>
</table>

\[ \Gamma_2 = -0.7782 - 0.04394m + 0.01126m^2 - 0.0001148m^3 \] (19)

where \( m \) is the molality of HCl in solution. The results of our calculations are shown as solid lines in Figure 3, and the dashed lines were taken from Fritz and Fuget [1956]. There is good agreement between measurements and calculations. This comparison shows that our low temperature extrapolation from room temperature data worked reasonably well in describing the thermodynamic properties for the HCl/H₂O system.

Table 6. Temperature Coefficients for HNO₃ Molality

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>( b_0 )</th>
<th>( b_1 )</th>
<th>( b_2 )</th>
<th>( b_3 )</th>
<th>( b_4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_{SO_2} )</td>
<td>-9.3085785070e-1</td>
<td>1.1200784716e+0</td>
<td>-8.759422370e-2</td>
<td>5.290261722e-4</td>
<td>-3.6297845637e+10</td>
</tr>
<tr>
<td>( a_{NO_2} )</td>
<td>-9.9276927926e+0</td>
<td>1.3861173987e-1</td>
<td>-7.5302479666e-4</td>
<td>1.905357417e-6</td>
<td>-1.8847180104e+9</td>
</tr>
<tr>
<td>( a_{HNO_3} )</td>
<td>8.9976745608e+0</td>
<td>-1.1682398549e-2</td>
<td>6.1056822242e-5</td>
<td>-1.5085723503e-7</td>
<td>9.4436719799e-10</td>
</tr>
<tr>
<td>( a_{HCl} )</td>
<td>-3.838447725e+2</td>
<td>4.8922229154e-4</td>
<td>-2.5494288719e-6</td>
<td>6.3363502169e-9</td>
<td>-6.1901374001e+12</td>
</tr>
</tbody>
</table>

Read -9.8727713620e+1 as -9.8727713620 x 10^1.
Table 7. Pressure Coefficients for the Condensation Point of HNO₃/H₂O Solutions

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (x 10⁻²)</td>
<td>1.2891</td>
<td>1.2848</td>
<td>1.3093</td>
<td>1.3287</td>
<td>1.3285</td>
<td>1.3285</td>
<td>1.2956</td>
<td>1.2839</td>
<td>1.3300</td>
</tr>
<tr>
<td>B (x 10⁻⁴)</td>
<td>2.7006</td>
<td>2.7234</td>
<td>2.7883</td>
<td>2.8402</td>
<td>2.8521</td>
<td>2.8626</td>
<td>2.8077</td>
<td>2.7928</td>
<td>2.8901</td>
</tr>
</tbody>
</table>

A and B coefficients are valid for a HNO₃ vapor pressure range of 10⁻⁸ - 3 x 10⁻⁶ torr.

For a simple application, we have fitted the model-generated mean activity coefficient results for HCl into a polynomial function in HCl molality (m_HCl), using equations (5) - (7) and (19). This relation is given as

\[ \ln \gamma_H^T = \sum_{i=0}^{3} a_i(T)m_{HCl} \]  

where \( \gamma_H^T \) is the HCl mean activity coefficient, and \( a_i \) variables are temperature coefficients given in Table 5. Note that from here on, equation (20) instead of (5) through (7) is used to calculate the mean activity coefficient for HCl. The activity parameters for the HCl/H₂O system (Table 2) are valid up to only a molality of 16, which is insufficient for most stratospheric applications. Thus we derived new activity parameters for the HCl/H₂O system (Table 2) for molalities > 16 from the ternary vapor pressure measurements over the H₂SO₄/HCl/H₂O system [Zhang et al., 1993a] described below. Further, because HCl has a low solubility in sulfuric acid solutions under stratospheric conditions, its impact on the equilibrium water vapor pressure over these solutions is negligible. Therefore, the deliquescence behavior of the HCl/H₂O system has a negligible impact on the equilibrium composition of stratospheric aerosols compared to the H₂SO₄/H₂O and HNO₃/H₂O systems.

2.1.3. HBr/H₂O system. Experimental data on the vapor pressure of HBr over aqueous HBr solutions at low temperatures are currently lacking. The room temperature values are predicted accurately by the parameters given in Tables 1 through 4 [Brimblecombe and Clegg, 1988; Lide, 1990]. We carried out similar calculations to those of HCl and HNO₃ to investigate the solubility behavior of HBr at lower temperatures. For computations, we assumed the same dependence for T² as we did for HCl (equation (19)). Unfortunately, the activity parameters for the HBr/H₂O system are invalid under stratospheric conditions.

We made a few comparisons between the HCl and HBr system over the range where the HBr parameters are valid. First, comparing the overall solubility constant of HBr and HCl at room temperature (Kₛ of HBr ~ 1000 x Kₛ of HCl) to that at 200 K (Kₛ of HBr ~ 10000 x Kₛ of HCl) shows that HBr's solubility increases more rapidly with a temperature decrease than HCl's does. Second, the mean activity coefficient of HBr and HCl in solution appear to differ by at most a factor of 10, for an electrolyte molality of about 10. Therefore the mean activity of HBr can be estimated roughly from the mean activity of HCl for cases where the activity parameters of HBr are not valid. Here we made a few assumptions to calculate the HBr mean activity (using the HCl mean activity coefficient times a constant), in order to estimate the solubility of HBr in H₂SO₄ solutions, described below.

2.2. H₂SO₄/H₂O System

H₂SO₄ in water is a multicomponent electrolyte system in itself. Thus the binary strong electrolyte model discussed

![Figure 2](image-url)  
**Figure 2.** The condensation point of aqueous HNO₃ solutions as a function of H₂O and HNO₃ vapor pressures calculated from (18).

![Figure 3](image-url)  
**Figure 3.** HCl vapor pressure over aqueous HCl solutions of various HCl contents. HCl solution molalities are indicated in the figure. Model results are shown as solid lines, and dashed lines are taken from Fritz and Fuget [1956].
above is not applicable to this system. However, Pitzer et al. (1977) have successfully treated the thermodynamics of aqueous H$_2$SO$_4$ as a mixture of H$^+$, HS O$_3^-$, and SO$_4^{2-}$ for concentrations up to 6 molal, and at temperatures close to 25°C. The Pitzer model for H$_2$SO$_4$ acid fails under stratospheric conditions for two reasons. First, the molality range for the Pitzer model corresponds to a 0.37% H$_2$SO$_4$ solution by weight, and stratospheric aerosols are usually more concentrated. Second, the Pitzer coefficients are valid for a temperature range of 0 to 50°C [Reardon and Beckie, 1987], which is out of the stratospheric range.

The thermodynamic properties of the H$_2$SO$_4$/H$_2$O system has been studied by Gmehl and Vermeulen [1964], Steele and Hamill [1981], Jaecker-Voirol et al. [1990] in the past, and more recently by Zelesnik [1991] and Zhang et al. [1993b]. A survey on the similarities and the differences between these various sources is given by Zhang et al. [1993b]. An important conclusion from the laboratory observations on the physical properties for H$_2$SO$_4$/H$_2$O solutions is that, for T < 210 K and H$_2$SO$_4$ weight percents < 60, the H$_2$SO$_4$ in solution is nearly completely dissociated into SO$_4^{2-}$ ion [Zhang et al., 1993b; Middlebrook et al., 1993]. We have used this conclusion to derive solute activity coefficients in the H$_2$SO$_4$/HNO$_3$/H$_2$O ternary system, described below.

Recently, Zhang et al. [1993b] have directly measured the water vapor pressure over an equilibrated H$_2$SO$_4$ solution (20-70 wt %) at low temperatures. We used their least squares fit for the variation of water vapor pressure over a known solution composition (only seven different compositions) to derive a deliquescence behavior for H$_2$SO$_4$/H$_2$O solutions. For simple application, we have fit the experimental results of Zhang et al. [1993b] into a polynomial function with respect to water vapor pressure ($P_w$) in units of torr, given by

$$W^a = \sum_{i=0}^{3} (-1)^i S_i (T) P_w^i$$

where $W^a$ is the weight percent for a pure binary sulfuric acid solution, and the $S_i$ variables are the temperature coefficients given in Table 8. The accuracy of the $S$ coefficients can be increased with more measurements. Note that (21) is valid only for the range where the measurements were carried out (20-70 H$_2$SO$_4$ wt % at 190-240 K). For higher temperatures, where solutions become more concentrated, equation (21) has less accuracy. Thus for stratospheric applications, we do not recommend using (21) for T > 210 K. Further, we have calculated the binary mean activity coefficient for the H$_2$SO$_4$/H$_2$O system under stratospheric conditions from the activity coefficient data for the HNO$_3$/H$_2$O system [Hammer and Wu, 1972] and the thermodynamic data for the ternary system of H$_2$SO$_4$/HNO$_3$/H$_2$O [Zhang et al., 1993a]. The method of calculation is discussed under the multicomponent electrolyte solution section. The results were fitted into a polynomial function in H$_2$SO$_4$ molality ($m_s$), given as

$$\ln \gamma_s^a = \sum_{i=0}^{3} a_i (T) m_s^i$$

where $\gamma_s^a$ is the H$_2$SO$_4$ mean activity coefficient, and $a_i$ variables are temperature coefficients given in Table 5.

3. Multicomponent Strong Electrolyte Systems

In principal, the activity coefficient for each electrolyte in a multicomponent system depends on the concentration of all the other species in solution. Thus for a mixed system the equilibrium relation for each binary component from (2) is

$$K_s = \frac{m(H^+) m(A^-) \gamma_{HA}^{mix}}{\rho_H}$$

where $\gamma_{HA}^{mix}$ is the mixed activity coefficient for electrolyte HA in the multicomponent solution. To express $\gamma_{HA}^{mix}$ for each electrolyte in solution as a function of molality of all other electrolytes in solution is difficult. Thus several researchers have developed empirical methods to calculate the mixed binary activity coefficients from the pure mean binary activity coefficients of all the solutes present in solution [e.g., Bromley, 1973; Kusik and Meissner, 1978]. Such methods have been applied in equilibrium models to predict the composition of tropospheric aerosols [e.g., Stelson and Seinfeld, 1982; Bassett and Seinfeld, 1983; Pillinis and Seinfeld, 1987].

For the systems of interest here, sulfate/nitrate aerosols, Bassett and Seinfeld [1983] showed that the empirical mixing rule of Kusik and Meissner (1978) adequately correlates to experimental data. This rule for the mixed binary activity coefficient ($\gamma_{12}^{mix}$) is expressed as

$$\ln \gamma_{12}^{mix} = \frac{z_1}{I(z_1 + z_2)} \left[ m_2 Z_2^2 \ln \gamma_{12}^{a_1} + m_2 Z_2^2 \ln \gamma_{12}^{a_2} + \cdots \right] + \frac{z_2}{I(z_1 + z_2)} \left[ m_1 Z_1^2 \ln \gamma_{12}^{a_1} + m_1 Z_1^2 \ln \gamma_{12}^{a_2} + \cdots \right]$$

Table 8. Temperature Coefficients for H$_2$SO$_4$ Weight Percent

<table>
<thead>
<tr>
<th>Coefficients</th>
<th>$S_0$</th>
<th>$S_1$</th>
<th>$S_2$</th>
<th>$S_3$</th>
<th>$S_4$</th>
<th>$S_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_0$</td>
<td>4.9306007769e+0</td>
<td>-2.8124576227e+2</td>
<td>3.6171943540e+4</td>
<td>-7.392108947e+5</td>
<td>-1.1640936469e+8</td>
<td></td>
</tr>
<tr>
<td>$S_1$</td>
<td>-1.6902946223e+1</td>
<td>5.7843291724e+3</td>
<td>-1.2462848248e+5</td>
<td>3.132502591e+7</td>
<td>-2.2068275308e+9</td>
<td></td>
</tr>
<tr>
<td>$S_2$</td>
<td>3.9722280419e+1</td>
<td>1.2350607474e+4</td>
<td>-3.4299494505e+7</td>
<td>6.2642386972e+8</td>
<td>-3.9709649439e+8</td>
<td></td>
</tr>
<tr>
<td>$S_3$</td>
<td>5.5968384906e+1</td>
<td>1.2923215128e+4</td>
<td>1.3504086346e+6</td>
<td>-1.7890533680e+8</td>
<td>8.8498119334e+8</td>
<td></td>
</tr>
<tr>
<td>$S_4$</td>
<td>8.2938840352e+1</td>
<td>2.0792294414e+4</td>
<td>2.9469683691e+7</td>
<td>8.8498119334e+8</td>
<td>1.0884875646e+9</td>
<td></td>
</tr>
<tr>
<td>$S_5$</td>
<td>1.0647596744e+2</td>
<td>2.7525067463e+4</td>
<td>4.2061852240e+5</td>
<td>-5.1877378665e+7</td>
<td>2.2849838182e+9</td>
<td></td>
</tr>
</tbody>
</table>

Read 4.9306007769e+0 as 4.9306007769 x 10$^0$. 

$\ln S_i (T) = a_0 + a_1 / T + a_2 / T^2 + a_3 / T^3 + a_4 / T^4$
where the odd and even subscripts refer to cations and anions, respectively, and $Z_i = (z_i + z_j) / 2$. $\gamma_{ij}$ is the pure mean binary activity coefficient for a solution containing only ions $i$ and $j$ at the same ionic strength $I$, given as

$$I = \frac{1}{z} \sum_i z_i^2 m_i$$

(25)

where $Z_i$ is the absolute value of the charge on species $i$, and $m_i$ is its molality. Thus to find the activity coefficients in the multicomponent solution with this method one needs to know the binary activity coefficients of all possible pairs of anions and cations in a solution of the same ionic strength.

In atmospheric applications, the water activity in the aqueous phase is equal to the ambient relative humidity. Using this fact along with the Gibbs-Duhem relation for the condition of equilibrium, Stokes and Robinson [1965] showed that

$$\sum m_k Z_k = 1$$

(26)

where $m_k$ is the molality of electrolyte $k$ in the multicomponent solution and $m_k^0$ is the pure binary molality calculated at the given ambient relative humidity. We determined the $m_k^0$ functions for $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ binary solutions for a wide range of stratospheric relative humidities, as described above. Including the water equation (26) in the equilibrium calculations discussed below assures that the computed aerosol compositions are in equilibrium with respect to water vapor.

To calculate the equilibrium composition for a multicomponent aqueous system, we solved the following equations simultaneously: (1) the solubility of each electrolyte from (23), (2) the mixed activity coefficients evaluated at $I$ for each electrolyte from (24), (3) the ionic strength from (25), and (4) the water equation at a given humidity from (26). To solve the equations, we used a numerical method described by M. Z. Jacobson et al. (submitted manuscript). This method conserves mass and charge, requires iteration but always converges. The advantage of this method, compared to one using a Newton-Raphson technique, is that it always converges and does not require a first guess.

### 3.1. $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ System

For this system, we used the ternary equilibrium vapor pressure measurements for $\text{HNO}_3$ over $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ solutions [Zhang et al., 1993b], and the mixed electrolyte model (equation (24)) to derive the mean pure binary activity coefficient of $\text{H}_2\text{SO}_4$. In this ternary system, the mixed activity coefficient for $\text{HNO}_3$ ($\gamma_{\text{HNO}_3}$) in solution is related to the $\text{HNO}_3$ vapor pressure ($P_{\text{HNO}_3}$), $\text{H}_2\text{SO}_4$ molality ($m_s$), and $\text{HNO}_3$ molality ($m_n$) from (23), by

$$\gamma_{\text{HNO}_3}^{-m} = \left(\frac{P_{\text{HNO}_3} K_s(T)}{m(\text{NO}_3^-) m(\text{H}^+)}\right)^{0.2}$$

(27)

Assuming that $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ are completely dissociated into $\text{H}^+$, $\text{SO}_4^{2-}$, and $\text{NO}_3^-$, the ion molalities in solution are $m(\text{NO}_3^-) = m_n$, $m(\text{H}^+) = m_n + 2m_s$ and $m(\text{SO}_4^{2-}) = m_s$. The nearly complete dissociation of $\text{H}_2\text{SO}_4$ into $\text{SO}_4^{2-}$ under low temperatures was discussed above. Using (27), and Zhang et al.'s [1993a] measurements of $\text{HNO}_3$ vapor pressure over a known ternary solution composition, $\gamma_{\text{HNO}_3}^{-m}$ can be calculated. Also, from (24), $\gamma_{\text{HNO}_3}^{-m}$ for this ternary system is

$$\ln \gamma_{\text{HNO}_3}^{-m} = \frac{1}{2I} \left[ 2(m_n + m_s) \ln \gamma_{\text{HNO}_3}^{-m}(T, I) + 2.25m_s \ln \gamma_{\text{HNO}_3}^{\text{H}_2\text{SO}_4}(T, I) \right]$$

(28)

where $I = m_n + 3m_s$ from (25). Knowing the $\gamma_{\text{HNO}_3}^{-m}$ from (28), and $\gamma_{\text{HNO}_3}^{\text{H}_2\text{SO}_4}$ from (15), $\gamma_{\text{HNO}_3}^{-m}$ can be calculated. We calculated the $\gamma_{ij}$ for all the laboratory cases studied by Zhang et al. (1993a), and fitted the mean pure activity coefficient data for $\text{H}_2\text{SO}_4$ into a polynomial function in sulfuric acid molality given in equation (22). Further, we recalculated the vapor pressure of $\text{HNO}_3$ over a known ternary solution composition from (27), using (15), (22), (28). The model results are shown as solid lines in Figure 4, and the dashed lines are the least squares fits from Zhang et al.

Under stratospheric conditions, the composition of the pure $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ system can be calculated by solving the equilibrium system, described above, for typical abundances of $\text{H}_2\text{SO}_4$, $\text{HNO}_3$, and $\text{H}_2\text{O}$. Note that for this system, (26) reduces to

$$m_n^0 + m_n^0 = 1$$

(29)

where $m_n^0$, $m_n^0$ are calculated at a given relative humidity from (17) and (21), $m_s$ and $m_n$ are the unknown equilibrium ternary compositions. We assumed that $\text{H}_2\text{SO}_4$ is present only in the aqueous phase ($\text{H}_2\text{SO}_4(gas) \sim 0$), and the relative humidity stays constant at a given temperature. Thus removal of water vapor by the aerosol phase is neglected ($\text{H}_2\text{O}(gas) \sim \text{const}$), which is true for all stratospheric conditions. Model results are shown in Figure 5 for two constant water vapor pressure profiles at ~ 20 km. It is clear that for temperatures below 200 K, $\text{HNO}_3$ is a major component of stratospheric aerosols. In addition, the solubility behavior of $\text{HNO}_3$ in stratospheric aerosols can be divided into three distinct regions (see Figure 5). In region a, $\text{HNO}_3$ is sparsely soluble. In region b, $\text{HNO}_3$ solubility in solution (1-10 m) is comparable to $\text{H}_2\text{SO}_4$, and in region c, $\text{HNO}_3$ becomes the major component. However, laboratory studies have shown that these ternary systems may freeze in region b or c, which could lead to the nucleation of NAT clouds [Molina et al., 1993]. In a separate paper we investigate the possibility for the existence of supercooled $\text{HNO}_3/\text{H}_2\text{O}$ solutions (region c in Figure 5) under stratospheric conditions (A. Tabazadeh et al., A study of Type I polar stratospheric cloud formation, submitted to Geophysical Research Letters, 1994).

Once the equilibrium compositions are known, the effective Henry's constant can be calculated from

$$H^*(T, m_n, m_s) = m_n \frac{K_s(T)}{(m_n + 2m_s)^2}$$

(30)

where $\gamma_{\text{HNO}_3}^{-m}$ is given by (28). Using the above relation, $H^*$ was plotted as function of $T$ for typical abundances of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ at about 20 km. The results are shown in Figure 6 for two constant water vapor pressure profiles. Note that $H^*$ depends on the $\text{HNO}_3$ molality ($m_n$) in a complicated fashion. For example, doubling the $\text{HNO}_3$ abundance in the gas phase would not simply double the aqueous $\text{HNO}_3$ concentration.
Thus it is not possible to express the $H^*$ for HNO$_3$ in stratospheric aerosols only as a function of sulfuric acid molality and $T$. However, in region a, where $m_H = 0$, there is a linear dependence between the concentration of HNO$_3$ in the gas and the aqueous phases (Figure 5).

### 3.2. H$_2$SO$_4$/$\text{HCl}/\text{H}_2\text{O}$ System

HCl solubility in sulfuric acid solutions has been recently measured by Zhang et al. [1993a]. They determined the equilibrium vapor pressure for HCl over ternary solutions of H$_2$SO$_4$/HCl/H$_2$O. As indicated above, the pure mean binary activity coefficient for HCl ($\gamma_{\text{Cl}}^{\text{mix}}$) is valid up to only 16 molal (Table 2). Thus we used the same procedure as described above to estimate the $\gamma_{\text{Cl}}^{\text{mix}}$ for molalities > 16. Using equations (20) and (23), we recalculated the vapor pressure of HCl over this ternary system. Model results are shown as solid lines in Figure 7, and the dashed lines are the least squares fit taken from Zhang et al.

The equations for solving the solubility of HCl in sulfuric acid solutions under stratospheric conditions can be greatly simplified. First, from laboratory observations, the solubility of HCl in sulfuric acid solutions is rather small ($m_{\text{Cl}} < 1$). Thus $m_{\text{Cl}}/m_{\text{Cl}}^0 = 0$ (where $m_{\text{Cl}}^0$ is the pure HCl molality in the binary system, see above), and $m_{\text{Cl}} = m_{\text{Cl}}^0$ from (26). Substituting these relations into (23) and (24), the $H^*$ for HCl in pure binary sulfate aerosols is

$$H^*(T, m_{\text{Cl}}^0) = \frac{m_{\text{Cl}}}{P_{\text{HCl}}} = \frac{K_{\text{Cl}}(T)}{2m_{\text{Cl}}^{0}\left[\gamma_{\text{Cl}}^{\text{mix}}(T, m_{\text{Cl}}^0)\right]^2} \quad (31a)$$

$$\ln \gamma_{\text{Cl}}^{\text{mix}} = \frac{1}{2f}\left[m_{\text{Cl}}^0\left(2\ln \gamma_{\text{Cl}}(I, T) + 2.25\ln \gamma_{\text{Cl}}^{\text{mix}}(I, T)\right)\right] \quad (31b)$$

where $f = 3m_{\text{Cl}}^0$, and we assumed that the first term in equation (24) is ~ 0. Using (31), the solubility of HCl in stratospheric sulfate aerosols can be calculated for a wide range of stratospheric humidities. The results are shown in Figure 6 for two constant water vapor pressure profiles.

---

**Figure 4.** HNO$_3$ vapor pressure over aqueous H$_2$SO$_4$/HNO$_3$/H$_2$O solutions of various HNO$_3$ and H$_2$SO$_4$ contents. Weight percents are indicated for each panel in the chart. Model results are shown as solid lines, and dashed lines are taken from Zhang et al. [1993a].

**Figure 5.** HNO$_3$ molality in aqueous H$_2$SO$_4$ solutions as a function of temperature. Model results are shown for two constant H$_2$O vapor pressure profiles as indicated in the chart. For model simulations, HNO$_3$ gas phase concentration was assumed to be $2.0 \times 10^{-7}$ torr. See text for description of various regions labeled in the figure.
3.3. HNO₃/HCl/H₂O System

Here we compare the ternary system of H₂SO₄/HCl/H₂O to that of HNO₃/HCl/H₂O. Although the HNO₃/HCl/H₂O system has not been studied in the laboratory under stratospheric conditions, we have the activity data required to predict HCl solubility in this ternary system. If we assume that stratospheric aerosols are pure HNO₃/H₂O solutions, then the solubility of HCl is approximately

\[ H'(T, m_{HCl}, m_{H}) = \frac{m_{HCl}}{P_{HCl}} = \frac{K_s(T)}{m_{H}^* \gamma_{HCl}^{mix}(T, m_{H}, m_{HCl})^2} \]  

(32a)

\[ \ln \gamma_{HCl}^{mix} = \frac{1}{2I} \left[ (2m_{H} + m_{N}) \ln \gamma_{HCl}^{mix}(I, T) + m_{H} \ln \gamma_{H}^{mix}(I, T) + 2.25m_{H} \ln \gamma_{H}^{mix}(I, T) \right] \]  

(32b)

and \( I = m_{H}^* \). Using (31) and (32), we plotted \( H' \) for HCl as a function of temperature in Figure 8. Depending on the humidity and temperature, HCl solubility can be either higher or lower in pure HNO₃/H₂O solutions than in H₂SO₄/H₂O solutions. In the regions of Figure 8 where the solubility of HCl is lower in pure HNO₃/H₂O solutions, actual stratospheric aerosols have insignificant amounts of HNO₃ in the aqueous phase (see Figure 5). Thus HNO₃ in solution will have no impact on HCl solubility. However, in regions where HCl has a higher solubility in pure HNO₃/H₂O solutions, the HNO₃ in solution could perhaps increase the HCl solubility.

3.4. H₂SO₄/HNO₃/HCl/H₂O System

We have solved this system following the procedures outlined above. The effective Henry's constant of HCl is then given by

\[ H'(T, m_N, m_{HCl}) = \frac{m_{HCl}}{P_{HCl}} = \frac{K_s(T)}{(m_N + 2m_{H}) \gamma_{HCl}^{mix}(T, m_N, m_{HCl})^2} \]  

(33a)

\[ \ln \gamma_{HCl}^{mix} = \frac{1}{2I} \left[ (2m_{H} + m_{N}) \ln \gamma_{HCl}^{mix}(I, T) + m_{N} \ln \gamma_{N}^{mix}(I, T) + 2.25m_{N} \ln \gamma_{N}^{mix}(I, T) \right] \]  

(33b)

where \( I = 3m_{H} + m_{N} \). Using the results from the two previous sections and our calculation for this quaternary system, we made a few conclusions about HCl dissolution. The solubility can be well described by (31), where H₂SO₄ is still a major component of the aerosol. Thus so long as H₂SO₄ limits HNO₃ dissolution, HCl solubility is not much different in the H₂SO₄/HCl/H₂O system than it is in the H₂SO₄/HNO₃/H₂O system. But, when HNO₃ is the major component of the aerosol, HCl solubility could be higher compared to the predictions from (31). In such cases, the solubility of HCl must be directly computed from (33).

3.5. H₂SO₄/HBr/H₂O System

This system has not been studied as extensively in the laboratory as the HCl and HNO₃ ternary systems in H₂SO₄ solutions. The only available measurement suggests that, for...
Figure 8. Effective Henry's law constant for HCl as a function of temperature in pure binary solutions of H$_2$SO$_4$/H$_2$O (solid lines) and HNO$_3$/H$_2$O (dashed lines) systems. Solid lines are calculated from (31), and dashed lines from (32); see text for detail. Model results are shown for two constant H$_2$O vapor pressure profiles as indicated in the chart. For model simulations, HNO$_3$ gas phase concentration was set at 2.0 x 10$^{-7}$ torr.

H$_2$SO$_4$ weight percents > 60 and temperatures > 220 K, HBr is at least 100 times more soluble than is HCl (L. R. Williams, private communication, 1994). Therefore it is reasonable to assume that HBr is significantly more soluble in stratospheric aerosols than is HCl.

We have made a few assumptions about the mean pure binary activity of HBr in order to estimate its solubility in H$_2$SO$_4$ solutions. As stated above, current HBr binary activity data are not valid for stratospheric applications. However, by comparing the mean binary activity (equation (5)) of HCl with that of HBr in the limit where HBr coefficients are valid, we estimate that $\gamma_{\text{HBr}} \approx 10^{2}$ (for the higher molalities). Using this relation in (23) and (24), the $H^*$ for HBr can be approximated from

$$H^*(T) = H(T) \cdot \left( \frac{K_s(T)}{m(H^*)} \right)$$

where $\gamma_{\text{HBr}} \approx 10^{2}$, and $\gamma_{\text{HCl}}$ is given by (31b). Note at $\sim$ 200 K, $K_s$ for HBr is about 10,000 times larger than the $K_s$ for HCl from (4). Thus, even though (34) is only a crude approximation, HBr is roughly 1000 times more soluble than is HCl in H$_2$SO$_4$ acid solutions for weight percents < 60 and T < 210 K (where it is reasonable to assume that H$_2$SO$_4$ is dissociated completely into SO$_4^{2-}$, see above). Model results for $H^*$ of HBr are shown in Figure 6. Preliminary results suggest that HBr and HCl will at least have comparable aqueous phase concentrations in stratospheric aerosols despite the fact that HBr column abundance is about 1000 times less than that of HCl. Equilibrium measurements for the HBr ternary system, similar to that for the HCl [Zhang et al., 1993a], are highly desirable, for improving our understanding on the solubility behavior of HBr in stratospheric aerosols.

4. Weak Univalent Acids in Aqueous Solutions

For weak acids in aqueous solutions, the strong electrolyte model is not applicable because there is a considerable amount of dissociated acid in solution. In the case of univalent weak acids, the dissolution in water leads to

$$HA(g) \rightleftharpoons HA(aq)$$

$$HA(aq) \rightleftharpoons A^- (aq) + H^+ (aq)$$

where $H$ is the physical Henry's law constant (mol/kg-atm), and $K_s$ (mole/kilogram) is the dissociation constant. From (35), the effective Henry's law constant ($H^*$) is [Seinfeld, 1986]

$$H^*(T) = H(T) \cdot \left( 1 + \frac{K_s(T)}{m(H^*)} \right)$$

where $m(H^*)$ is the molality of the H$^+$ ion in solution. Note that the effect of dissociation is to "pull" more acid into solution than predicted on the basis of the physical Henry's law solubility alone. Therefore from $K_s$, $H$, and the pH of the solution, $H^*$ can be estimated. Below, we discuss the applicability of (36) to the dissolution of HF and HOCI in H$_2$SO$_4$ solutions.

4.1. H$_2$SO$_4$/HF/H$_2$O System

The solubility of HF in an aqueous solution can be estimated from (36), where the temperature dependent-functions are

$$\ln H(T) = 6.61712 + 3360.464/T - 0.02789T$$

$$\ln K_a(T) = -12.6558 + 1599.7113/T$$

These functions were derived from the enthalpy and the heat capacity change for reactions (35a) and (35b), and the standard temperature values for $H$ and $K_a$ [Pitzer, 1991; Haung, 1989; Nordstrom et al., 1990].

For slightly acidic (pH > 4), neutral or basic pH, the dissociation of HF in solution can increase the solubility, which can be calculated from (36) and (37). However, for highly acidic solutions, the dissociation of HF has almost no impact on the HF solubility. Thus if (36) holds, then $H^* = H$. Due to lack of experimental data on the solubility of HF in concentrated H$_2$SO$_4$ solutions, we suggest using (37a) for calculating the solubility of HF in H$_2$SO$_4$ solutions. The variation of $H$ with respect to temperature is depicted in Figure 6 based on equation (37a).

4.2. H$_2$SO$_4$/HOCI/H$_2$O System

HOCI, like HF, is a weak acid, and its solubility in aqueous solutions can be estimated from (36). The physical Henry's constant for HOCI has been measured by Blatchley et al. [1992], and is equal to 16.677 atm$^{-1}$ at 20°C. Here the Henry's constant ($H_*$) expresses the mole fraction (X) of HOCI over the equilibrium vapor pressure of HOCI, where $H = 1000H_* / 18$ for $X < 1$. Using the heat of formation for HOCI in the gas [Chase, 1985] and the aqueous phase [Lide, 1990], the temperature dependence of the physical Henry's constant can be estimated from

$$\ln H = -10.989 + 5220.973/T$$
The effective Henry's law constant can now be calculated from (36). However, we could not find any data on the heat of formation for the OCl\(^-\) ion in the aqueous phase. Thus we were unable to estimate the temperature dependence for the dissociation constant. Therefore the effective Henry's law constant for HOCI can not be estimated at other temperatures.

Using the same arguments as above, we predict that in highly acidic solutions, the dissociation of HClO has no impact on its solubility, and HClO solubility can be estimated from (38). But recently, Hanson and Ravishankara [1993] determined the effective Henry's law constant for HClO in H\(_2\)SO\(_4\)/H\(_2\)O solutions and showed that the solubility appears to depend on H\(_2\)SO\(_4\) weight percent. However, the dependence of solubility on the H\(_2\)SO\(_4\) weight percent, where \(m(\text{H}^+) > 1\) for all cases studied (Hanson and Ravishankara, 1993), can not be related to the acidity of the solution since \(K_a / m(\text{H}^+) < 1\) (equation (36)). Therefore, from laboratory measurements, (35a) and (35b) are not adequate steps for describing the dissolution mechanism of HClO in concentrated H\(_2\)SO\(_4\) solutions.

From laboratory measurements [Hanson and Ravishankara, 1993], we suggest the following steps for dissolution of HClO in concentrated H\(_2\)SO\(_4\) acid solutions

\[
\text{HClO(gas)} \xrightarrow{H_{\text{acid}}} \text{HClO(acid)}
\]  

\[
\text{HClO(acid)} + \text{SO}_4^{2-} (\text{acid}) \xrightarrow{K_{\text{acid}}} \text{HSO}_4(\text{acid}) + \text{OCl}^- (\text{acid})
\]

where we used the "acid" notation for solubility in H\(_2\)SO\(_4\) solutions to distinguish it from the "aq" which refers to dissolution in the aqueous solution. \(H_{\text{acid}}\) is the physical Henry's constant for a H\(_2\)SO\(_4\) solution at a given molality, \(m_s\), and \(K_{\text{acid}}\) is the dissociation constant in the sulfuric acid solution. From the steps above, the effective Henry's law constant is

\[
H^\ast_{\text{acid}} = H_{\text{acid}}(T,m_s) \left(1 + \frac{K_{\text{acid}}(T)m(\text{SO}_4^{2-})}{m(\text{HSO}_4^-)}\right)
\]

where the solubility depends on the molality ratio of the bisulfate ion to the hydrogen sulfate ion. Note that as the H\(_2\)SO\(_4\) solution becomes more concentrated, this ratio becomes smaller and \(H^\ast_{\text{acid}}\) approaches \(H_{\text{acid}}\). Of course, to make predictions for HClO solubility from (40), the physical Henry's constant and the dissociation constant must be determined in H\(_2\)SO\(_4\) solutions from laboratory measurements. However, this formulation can explain the dependence of HClO solubility, as observed by Hanson and Ravishankara [1993]. We have approximately fitted the \(H^\ast_{\text{acid}}\) data from Hanson and Ravishankara to a linear function in H\(_2\)SO\(_4\) molality \(m_s\), given as

\[
\ln H^\ast(T,m_s) = A_0 + A_1 m_s + A_2 m_s^2 + A_3 m_s^3
\]

where \(A\) coefficients are given in Table 9. Figure 9 shows the calculated values of \(H^\ast\) for a number of H\(_2\)SO\(_4\) solutions from (41). The dashed line shows the solubility predicted by HOCI dissolution in an aqueous solution from (38). Thus for less concentrated solutions (< 45 % H\(_2\)SO\(_4\) by weight), H\(_2\)SO\(_4\) might enhance the solubility of HClO. For simple application to the stratosphere, the \(H^\ast\) for HClO can be computed by substituting (21) into (41). Results of calculation for the \(H^\ast\) of HClO in aqueous H\(_2\)SO\(_4\) solutions are shown in Figure 6.

5. Stratospheric Implications and Volcanic Effects

As shown above, the composition of stratospheric aerosols is very sensitive to the relative humidity. However, equilibrium compositions also vary as a function of the total amount of HNO\(_3\) and H\(_2\)SO\(_4\) present per unit volume of air. To study the impact of all variables involved, we calculated variations in the aerosol composition as a function of temperature for five different cases (Table 10). The results are shown in Figure 10, where case I is for a typical condition at ~ 16 km altitude. The solid lines are calculated from (21), and the dashed lines are calculated from solving the ternary system of H\(_2\)SO\(_4\)/HNO\(_3\)/H\(_2\)O, as described above.

Molina et al. [1993] have shown that ternary bulk solutions with similar compositions as shown in Figure 10 can freeze under laboratory conditions. Whereas, for equivalent aqueous H\(_2\)SO\(_4\) solutions (solid lines in Figure 10), the freezing temperature is observed to be near the ice frost point [Zhang et al., 1993b; Middlebrook et al., 1993]. The freezing of these ternary solutions may lead to the nucleation of NAT clouds in the stratosphere, as indicated by Molina et al.. In the laboratory, ternary bulk solutions (sample volumes ~ 5 \mu l - 5 ml) froze in about one hour when they were held at their equilibrium temperatures. In the atmosphere, the volume of a particle with a radius of about 1 \mu m is ~ 4 \times 10\(^{12}\) ml. According to the nucleation theory, the probability for homogeneous freezing of a solution depends strongly on the volume of the sample. The volume of the laboratory samples were about 10\(^4\) to 10\(^12\) times larger than the volume of a particle with a radius of ~ 1 \mu m. Therefore, it is possible for ternary droplets to remain supercooled instead of nucleating into NAT particles under stratospheric conditions. However, more work is needed to demonstrate such freezing of aerosols as suggested by Molina et al.. Below we discuss solubilities and reactivities of various species in stratospheric aerosols, assuming that aerosols remained supercooled above the ice frost point.

| Table 9. Effective Henry's Coefficients for HClO |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Coefficients    | \(a_0\)         | \(a_1\)         | \(a_2\)         | \(a_3\)         |
| \(A_0\)         | -3.8542280588e+1| 8.0306114742e+0 | -6.6982627997e-1| 1.8577458295e-2 |
| \(A_1\)         | 1.1723617497e+4 | -2.3102480134e+3| 1.9422695893e+2 | -5.4624379476e+0|

Read: -3.8542280588e+1 as -3.8542280588 \times 10^1.
5.1. Background Conditions

Figure 10a shows a typical composition of stratospheric aerosols at ~ 16 km altitude. From (18), the condensation point of the HNO₃/H₂O solutions for case I (Table 10) is about 195 K, which corresponds approximately to the maximum of the HNO₃ weight percent curve in Figure 10a. A comparison of Figure 10a with Figure 10b shows that lowering the HNO₃ concentration by one-half slightly changes the ternary aerosol composition, and the maximum for the weight percent of the HNO₃ curve is shifted by ~ 1 K. For case II, the condensation point of the HNO₃/H₂O solution is ~ 194 K from (18). For case III (Figure 10c), the water mixing ratio was decreased to one-half that for case I (Figure 10a). This results in a significant change in the aerosol composition, and the maximum of the HNO₃ weight percent curve is shifted by ~ 3 K compared to case I. The condensation point of the HNO₃/H₂O solution from (18) is ~ 192 K for case III. Therefore, it appears that, as the condensation point of the HNO₃/H₂O solution is approached, the background aerosols can rapidly uptake HNO₃. This HNO₃ uptake is also accompanied by H₂O vapor absorption, which results in the growth of background aerosols.

We also calculated the supersaturation (S) of HNO₃ over the NAT phase from Hanson and Mauersberger's [1988b] empirical equation for cases I through III, where S = 1 at ~ 199.6, 198.7, and 196.3 K, respectively. At these temperatures, the ternary aerosols contain < 10% HNO₃ by weight, and are ~ 4 K warmer with respect to the condensation point of HNO₃/H₂O solutions (Figure 10). As indicated above, as the condensation point of the HNO₃/H₂O solution is approached, aerosols can rapidly uptake HNO₃ and grow in size. If the aerosol is liquid when S = 1, then HNO₃ dissolution prevents the formation of a NAT embryo on the particle surface and therefore NAT can not grow from the gas phase onto the aerosol surface. From the NAT frost point (S ~ 1) to the intersection point (S ~ 10) in Figure 10 for cases I through III, the total HNO₃ uptake by the particles can contribute only slightly to the deliquescing of the background aerosols. But, from the intersection point to the ice frost point (~ 192.5 K for cases I and II; ~ 189 K for case III), the aerosols could grow to sizes that are significantly larger than those of the average background mode (about 0.1 μm radius) (A. Tabazadeh et al., submitted manuscript). Many Arctic field investigations showed that significant particle growth was not evident until S was about 10 [Dye et al., 1992; Kawa et al., 1992; Pueschel et al., 1992]. These apparent supersaturations were observed primarily because significant particle growth is expected to occur only for S values > 10, if the aerosols remain as supercooled droplets (A. Tabazadeh et al., submitted manuscript).

5.2. Volcanic Conditions

Figures 10d and 10e demonstrate aerosol compositions under volcanic conditions, where the background sulfur concentration is increased by a factor of 10 and 100, respectively. For cases IV and V, the HNO₃/H₂O condensation point is ~ 195 K; therefore, an increase in the HNO₃ uptake is noted at ~ 195 K. Under volcanic conditions aerosols contain more H₂SO₄ than they do under background conditions (case I). However, under drastic volcanic conditions (Figure 10e), there is a significant difference between volcanic aerosol and background compositions. Also, the sulfur burden is so high that the HNO₃ concentration never exceeds that of H₂SO₄ for the conditions assumed for case V (Figure 10e).

Observational data of Mount Pinatubo aerosols suggest that volcanic aerosols remained supercooled instead of freezing to

<table>
<thead>
<tr>
<th>Case</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO₃ mixing ratio, ppbv</td>
<td>10.0</td>
<td>5.0</td>
<td>10.0</td>
<td>10.0</td>
<td>10.0</td>
</tr>
<tr>
<td>H₂O mixing ratio, ppmv</td>
<td>5.0</td>
<td>5.0</td>
<td>2.5</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>H₂SO₄ total mass, μg/m³ of air</td>
<td>0.036</td>
<td>0.036</td>
<td>0.036</td>
<td>0.36</td>
<td>3.6</td>
</tr>
<tr>
<td>Total pressure, mbar</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Abbreviations ppbv and ppmv are parts per billion by volume and parts per million by volume, respectively.

---

**Figure 9.** Effective Henry's law constant for HClO as a function of temperature in aqueous H₂SO₄ solutions (solid lines). Solid lines are calculated from (41) based on Hanson and Ravishankara's data [1993], as described in the text. The dashed line is the pure aqueous physical Henry's law constant calculated from (38).
form NAT particles [Toon et al., 1993]. Pinatubo aerosols froze at ~190 K, which was near the ice frost point. In addition, recently Deshler et al. [1994] indicated that the physical characteristics of PSCs change significantly in the presence of volcanic aerosols. The PSC particles observed in Pinatubo clouds by Deshler et al. were usually < 1.0 μm in radius and more abundant than PSCs observed when volcanic aerosols were absent. These PSCs were probably ternary supercooled droplets instead of NAT particles, which are usually > 1.0 μm in radius. Hence, volcanic aerosols having similar compositions to the ones shown in Figure 10e may remain supercooled at temperatures above the ice frost point in the stratosphere.

5.3. Aerosol Scavenging

Assuming that H₂SO₄ is present only in the aerosol phase, the scavenging efficiency (r) of species X can be scaled with respect to the total mass of H₂SO₄ present per unit volume of air, given as

\[ r = \frac{L_{wc}m_xN_A}{X_g^o} \]  \hspace{1cm} (42a)

\[ L_{wc} = \text{mass}_x \times 10^{-12} / 98m_s \]  \hspace{1cm} (42b)

where \( L_{wc} \) is the total liquid water content (kg) present per cubic centimeter of air, \( X_g^o \) is the gas phase concentration of
species \( X \) (\#/cm\(^3\)), \( N_A \) is the Avogadro's number, \( m_X \) is the molality of species \( X \) in solution, \( m_s \) is total mass of \( H_2SO_4 \) (\( \mu g \)/m\(^3\) of air), and \( m_a \) is the molality of \( H_2SO_4 \) in the aerosol phase. Below, we used (42a) and (42b) to calculate the efficiency of stratospheric aerosols in the removal of gas phase species.

Using \( HNO_3 \) ternary compositions shown in Figure 10 in (42), we calculated the \( HNO_3 \) scavenging efficiency by stratospheric aerosols. The results are shown in Figure 11. For cases I, II, III, and IV (Table 10), the \( HNO_3 \) gas phase concentration decreases after the intersection point is reached in Figure 10. From the intersection point to the ice frost point (~192.5 K for cases I, II, and IV; ~189 K for case III), about 50% to 80% of the \( HNO_3 \) gas column can be scavenged by the aerosol phase (Figure 11). For case V, where the total mass of \( HNO_3 \) and \( H_2SO_4 \) present per unit volume of air is roughly equal (~3.5 \( \mu g \)/m\(^3\) of air), the \( HNO_3 \) column can be depleted by aerosols even at higher temperatures. From Figure 11, at about 196 K, the \( HNO_3 \) column is depleted by ~50%, observed by Toon et al. [1993]. In addition, Coffey and Mankin [1993] observed that, in the volcanic clouds of El Chichon and Pinatubo, the heterogeneous conversion of \( N_2O_5 \) into \( HNO_3 \) by volcanic aerosols did not correspond to an equal increase in the \( HNO_3 \) column abundance. This may be explained by the volcanic aerosol scavenging of \( HNO_3 \) for \( T \leq 200 \text{K} \).

The solubility of \( HCl \) in stratospheric aerosols is illustrated in Figure 12 for the cases mentioned above (Table 10). The solubilities were calculated directly from (33), using the \( H_2SO_4 \) and \( HNO_3 \) concentrations shown in Figure 10. \( HCl \) scavenging was calculated from (42a) and (42b) assuming \( X^* \) ~ \( 5 \times 10^9 \text{ /cm}^3 \). For cases I and II at 193 K, the \( H^* \) for \( HCl \) is ~ \( 10^8 \text{ mol} / \text{kg-atm} \), which is a factor of 5 larger than if a pure \( H_2SO_4/H_2O \) composition is assumed for the aerosols (Figure 12). We used \( H^* \) values for \( HCl \) shown in Figure 12 at 193 K to calculate the \( HCl \) solubility in solution. The calculated \( HCl \) molality in solutions is ~0.13 m. Using this molality in (42a) for cases I and II, ~6% of the \( HCl \) gas column can be scavenged by the aerosols at about 193 K. At 192.5 K (~ice frost point), ~12% of the \( HCl \) can be depleted from the gas phase by the aerosols. For case III, similar depletions of the \( HCl \) column (~6% to 12%) are calculated at about 189 K (~ice frost point) to 190 K.

For case VI at 193 K, the \( HCl \) solubility in solution (0.13 m) and the liquid water content are similar to that of case I. Thus, \( HCl \) column can be depleted by ~6% at 193 K and ~12% at 192.5 K. For case V, the \( HCl \) solubility (\( H^* \) ~ \( 3 \times 10^8 \text{ mol} / \text{kg-atm} \)) is lower in the volcanic aerosols than in aerosols described in case I. The calculated \( HCl \) solubility in solution for case V at 193 K is roughly 0.04 m. However, the liquid water content of the aerosols per unit volume of air is about 2.5 times larger for case V than for case I. Using this \( HCl \) solubility in (42a), the \( HCl \) column can be depleted by about 5% at ~193 K. However, as the temperature approaches the ice frost point (~192.5 K), the \( H^* \) can increase by a factor of 3, which can cause a 15% depletion of the \( HCl \) gas column. If ice does not crystallize at ~192.5 K in the volcanic aerosols, then the \( HCl \) column can be depleted by about 30% at ~192 K (Toon et al. [1993] observed a 30% depletion of the \( HCl \) column in the dense volcanic clouds of Pinatubo, which may be related to the volcanic aerosol scavenging of \( HCl \)). Further, they also suggested that the depletion of the \( HCl \) gas column could have been caused by the chemical processing of \( HCl \) in the volcanic aerosols, as described below. In fact, both factors (scavenging and chemical processing of \( HCl \)) may have contributed some to the depletion of the \( HCl \) column as observed by Toon et al. [1993].

The scavenging efficiency of \( HBr \) by stratospheric aerosols can be approximated from (34) and (42a). We emphasize that the accuracy of (34) must be validated against laboratory observations. Assuming \( X^* \) ~ \( 5 \times 10^6 \text{ /cm}^3 \) for the \( HBr \) gas phase concentration, the \( HBr \) gas column can be depleted by about 100% at ~192.5 K (ice frost point) for cases I, II, IV, and V. For case III similar depletions are calculated at ~189 K. The total mass of \( HBr \) in the stratosphere is about 5 \( \times 10^4 \mu g / \text{m}^3 \) of air, which is roughly 70 times smaller than the background \( H_2SO_4 \) mass (Table 10). Thus, even if all the \( HBr \) column is incorporated into the aerosols, the \( HBr \) aqueous
concentration is always roughly 70 times smaller than the H$_2$SO$_4$ aqueous concentration. For example, for case I at 193 K, the H$_2$SO$_4$ weight percent in solution is ~ 0.5% (Figure 10a). Therefore, if we assume that all the available HBr is in the aqueous phase, it can contribute only 0.0070 % to the total aerosol mass. However, the HBr aqueous concentration can be about 10$^5$ m, which may result in a rapid chemical processing of HBr, as described below.

In the case of many in situ measurements, the X/HF ratio is used as an indicator of the chemical removal of X [Toon et al., 1993]. This holds if HF is chemically inert. However, if considerable amount of HF is scavenged by the aerosol phase, the X/HF ratio should be modified. When calculating the scavenging efficiency of HF, it is important to note that (37a) might not be valid for acidic solutions. Due to a lack of laboratory data, we used (37a), and (42a) to estimate the scavenging efficiency of HF by stratospheric aerosols. From (37a), the aqueous phase Henry's constant for HF is ~ 10$^9$ mol / kg-atm (for T < 193 K), which we have used in (42a) to calculate the scavenging efficiency of HF. Assuming X$_H$ = 5 x 10$^4$ / cm$^3$ for the HF gas phase concentration, the calculated HF molality in solution is about 0.01 m for T < 193 K. For cases I through V (Table 10), the HF gas column can be depleted by ~ 1 % before the ice frost point is reached. However, if HF dissolution in H$_2$SO$_4$ solutions is similar to that of HOCI, then its effective Henry's constant could be a factor of 10 larger in dilute H$_2$SO$_4$ solutions (see Figure 9) compared to the pure aqueous phase physical Henry's constant used here. Therefore, up to a 10 % scavenging of HF by the aerosols at low temperatures may not be ruled out in case V. Under a volcanic condition, where H$_2$SO$_4$ aqueous concentration is significant at low temperatures, HF can reversibly react with sulfate ions in solution, increasing the solubility of HF. Laboratory observations on the solubility behavior of HF in aqueous HNO$_3$ and H$_2$SO$_4$ solutions are needed to narrow the uncertainty associated with using the X/HF ratio.

5.4. Chemistry in/on Supercooled Droplets

The HCl aqueous concentration in supercooled aerosols may be as high as 0.1 m, which may result in a rapid chemical processing of HCl in solution. Recently, Hanson and Ravishankara [1993] determined that the aqueous phase reaction rate constant for HCl + HOCI reaction is k ~ 10$^9$ L / mol-s (~ 10$^3$ kg of water / mol-s). Thus the reaction rate in the bulk can be computed as

\[ R = k[HCl][HOCI] \]  

(43)

where the bracketed quantities are aqueous phase concentrations.

For cases I and II, the liquid water content is ~ 4 x 10$^{-15}$ kg / cm$^3$ of air from (42b) and the HCl aqueous concentration is about 0.1 m at 193 K (assuming X$_H$ = 5 x 10$^4$ / cm$^3$). The HOCI solubility in solution at 193 K for cases I and II (almost pure HNO$_3$/H$_2$O solutions, see Figures 10a and 10b) may be lower than that estimated from (41) because HOCI in solution probably does not reversibly react with nitrate ions as it does with sulfate ions (see above). Therefore, we used (38) instead of (41) to calculate the HOCI Henry's law constant for cases I and II, which is ~ 10$^9$ mol / kg-atm (see the dashed line in Figure 9). For an HOCI gas phase concentration of about 10$^5$ / cm$^3$, the HOCI aqueous concentration is ~ 10$^5$ m. Hence from (43) and (42b), 2.4 x 10$^9$ Cl$_2$ molecules may be produced every second per cubic centimeter of air. Also, for volcanic conditions (case V), where the aerosols contain more H$_2$SO$_4$ in solution, the effective Henry's constant for HOCI may be a factor of 10 larger (~ 10$^3$ mol / kg-atm, see Figure 9). This can result in a rapid chemical processing of HCl in solution, which may have contributed some to the depletion of the HCl column, in the volcanic clouds of Pinatubo, as observed by Toon et al. [1993].

Hanson and Ravishankara [1991] have parameterized the reaction probability (number of molecules that react on the surface (or bulk) / gas kinetic flux) for the C1ONO$_2$ + H$_2$O reaction as a function of H$_2$SO$_4$ weight percent in solution (log $f_m = 1.86 - 0.0747W_s$, where $f_m$ is the reaction probability and $W_s$ is the weight percent of H$_2$SO$_4$ in solution). Assuming an aqueous H$_2$SO$_4$ composition for the droplets for case I (solid curve in Figure 10a), the H$_2$SO$_4$ weight percent varies from ~ 60 % at 206 K to ~ 36 % at 192.5 K (ice frost point). The reaction probability for the hydrolysis of C1ONO$_2$ increases by a factor 60 as the temperature decreases from 206 to 192.5 K. For conditions of case I, the relative humidity (RH = 100 x ambient water vapor pressure (torr) / equation (11)) varies from 7 to 43 % as the temperature decreases from 206 to 192.5 K. Therefore, increasing the RH over the aerosol surface by a factor of 6 can lead to an increase in the reaction efficiency by a factor of 60. Abbatt and Molina [1992] have observed that the efficiency of C1ONO$_2$ reactions on NAT surfaces also increased as the RH over the surface increased. Recently, we calculated that an increase in the RH over a NAT surface from 6.7 % to 50 % increased the efficiency of C1ONO$_2$ reactions on NAT surfaces by a factor of about one-hundred [Tabazadeh and Turco, 1993]. We attribute this to an increase in the abundance of adsorbed water layers on NAT surfaces.

From the similarities between reactions of C1ONO$_2$ on NAT and on aqueous H$_2$SO$_4$ surfaces described here, we conclude that C1ONO$_2$ hydrolysis probably occurs on the surface of H$_2$SO$_4$ solutions. Also, the reaction probability is controlled by the activity of water over the aerosol surface rather than the aerosol composition. Therefore, the reaction probability for this heterogeneous process calculated on pure aqueous H$_2$SO$_4$ solutions [Hanson and Ravishankara, 1991] is probably valid for all the ternary compositions shown if Figure 10 (ternary lines), as long as a weight percent of a pure aqueous H$_2$SO$_4$ solution (solid line in Figure 10) is assumed for the calculations.

Abbatt and Molina [1992] have shown that the reaction probability for the C1ONO$_2$ + HCl reaction is about 100 times larger than the C1ONO$_2$ + H$_2$O reaction on NAT surfaces. Under their laboratory conditions, HCl formed roughly a monolayer on NAT surfaces [Tabazadeh and Turco, 1993]. If C1ONO$_2$ reactions occur on the surface of H$_2$SO$_4$ acid solutions, then the efficiency for the C1ONO$_2$ + HCl reaction may be a factor of 100 larger than the C1ONO$_2$ + H$_2$O reaction. However, for a 0.1 m HCl solution (0.1 moles of HCl per 55.5 moles of H$_2$O), the HCl surface concentration is ~ 500 times smaller than the H$_2$O surface concentration. This is significantly different from the conditions on a NAT surface, where HCl forms roughly a monolayer on the surface. Assuming 500 collisions of C1ONO$_2$ molecules to an aerosol surface, only 1 collision will be with an HCl molecule (for a 0.1 m HCl solution). However, because the reaction with HCl is 100 times more efficient, about 20 % of the total number of effective
collisions with the surface may be the result of the direct HCl reaction with ClONO₂ (for 0.1 m HCl solution). If HCl concentration is 0.01 m, then only 2% of the effective collisions are due to the ClONO₂ + HCl reaction. For HCl concentration < 0.01 m, the direct reaction of the ClONO₂ + HCl on the surface may be negligible compared to the ClONO₂ + H₂O reaction.

The reaction probability for the hydrolysis of ClONO₂ on stratospheric aerosols is about 0.1 [Hanson and Ravishankara, 1991] at low temperatures, which rapidly produces HOCI on the aerosol surface. This heterogeneous process may significantly increase the HOCI pressure over the surface of a droplet and therefore increase the HClO concentration in solution, enhancing the rate of the Cl + HOCI bulk phase reaction, described above. In addition, we calculated an aqueous concentration for HBr of about 10³ m in the aerosols for T < 193 K (see above). Therefore, if we assume a bulk phase reaction rate constant of ~ 10⁶ L/mol-s for the HBr + HOCI reaction (same as that of the Cl + HOCI reaction), then this process may also contribute to the production of reactive halogen species.

6. Conclusions

In this paper we presented the first thorough study on the composition of stratospheric aerosols. Our results show that, for temperatures below 200 K, HNO₃ is a major component of stratospheric aerosols. Here we discussed some of the effects caused by HNO₃ dissolution on the physical and chemical properties of stratospheric aerosols. For instance, after large volcanic eruptions, such as Pinatubo, the composition of stratospheric aerosols may be different from background compositions. We predicted that these solutions do not freeze until at least the ice frost point is reached, and they may significantly scavenge HNO₃ and HCl from the gas phase. Further, in volcanically disturbed periods, different types of PSC particles (ternary solutions of H₂SO₄/HNO₃/H₂O) may exist. The chemistry occurring in these droplets may be quite different from the heterogeneous chemistry occurring on NAT surfaces. Currently, we are developing a model to describe the mechanism at which chlorine- and nitrogen-containing compounds react on both the surfaces and in the bulk of stratospheric aerosols. Previously, we constructed a surface-chemistry model to investigate the mechanism at which NAT and ice particles activated chlorine compounds [Tabazadeh and Turco, 1993]. These models are essential to aid our understanding, on the microscopic level, about the nature of physical-chemical processes responsible for the changes in the stratospheric composition and ozone abundance.

Acknowledgments. We wish to thank O. Toon, R. Zhang, M. Molina, A. Middlebrook, M. Tolbert, L. Williams, D. Golden, B. Luo, S. Clegg, T. Peter, R. Müller, P. Crutzen, D. Hanson, and A. Ravishankara for preprints of their work. This research was supported by NASA's Upper Atmosphere Program under grant NAGW-2183 and the NSF Atmospheric Chemistry program under grant ATM-9216646. One of us [AT] is supported by a NASA Graduate Fellowship in Global Change Research under grant NGR-50079.

References


Toon O. et al., Heterogeneous reaction probabilities, solubilities, and the physical state of cold volcanic aerosols, Science, 261, 1136-1140, 1993.

M. Z. Jacobson, A. Tabazadeh, and R. P. Turco, Department of Atmospheric Sciences, University of California, Los Angeles, 405 Hilgard Avenue, Los Angeles, CA 90024-1565.

(Received November 23, 1993; revised March 14, 1994; accepted March 22, 1994)