Laboratory Investigations of Heterogeneous Chemistry Important to Ozone Depletion in the Stratosphere

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Abstract

Results of laboratory investigations of heterogeneous chemistry important to ozone depletion in the stratosphere are presented. Thermodynamic properties (such as melting points, enthalpies of fusion, etc.) for acids which are present in the stratosphere (HCl, HNO₃, and H₂SO₄) are studied using laboratory-assembled apparatus of electrical conductivity and differential thermal analysis and using a commercial differential scanning calorimeter (DSC). Vapor pressures and infrared spectra of liquid and supercooled solutions, and of liquid-solid and solid-solid coexistence mixtures for the HCl/H₂O and H₂SO₄/H₂O binary systems are investigated. Equilibrium constants and standard enthalpies of formation for the pure crystalline hydrates of those acids as well as their corresponding liquid compositions are determined from the vapor pressure and calorimetric data. A theoretical approach, which allows determination of vapor pressures for two adjacent hydrates in thermodynamic equilibrium and for the coexistence systems involving a hydrate and ice in a binary system, is presented in terms of chemical equilibrium principles and compared with the experimental data for thermodynamic consistence.

Vapor pressures of HNO₃ and HCl over H₂SO₄/HNO₃/H₂O and H₂SO₄/HCl/H₂O solutions as well as over H₂SO₄/HNO₃/HCl/H₂O solutions are also measured in order to predict incorporation of stratospheric acids into the background sulfate aerosols. From the data, the Henry’s law solubility constants for those systems are determined and the equilibrium compositions of aqueous stratospheric aerosols are predicted as a function of ambient temperature and mixing ratios of H₂O and HNO₃. The results indicate that at the low temperatures characteristic of the stratosphere at high latitudes in the winter and spring, the HNO₃ content reaches levels of the order of 10% wt in the background sulfate aerosols. The results also reveal that the amount of dissolved HCl in the background sulfate aerosols is small when compared with dissolved HNO₃, but may be significant for the production of Cl₂ via the heterogenous reaction between ClONO₂ and HCl at low temperatures.

The identity of crystallized H₂SO₄/HNO₃/H₂O ternary solutions is examined from the vapor pressure measurements, along with infrared spectroscopic and DSC data, showing that freezing of supercooled H₂SO₄/HNO₃/H₂O solutions leads to the formation of a solid mixture

2
consisting of nitric acid trihydrate (NAT) crystals and sulfuric acid tetrahydrate (SAT) crystals. A new mechanism for type I PSC formation is proposed and shown to reconcile many atmospheric observations.

Finally, a high sensitivity molecular beam (modulated) quadrupole mass spectrometer coupled to a fast-flow reactor is employed to study heterogeneous reaction probabilities of ClONO₂ and HCl on water-ice, nitric acid hydrates, and sulfuric acid hydrates. In particular, the results reveal that frozen background sulfate aerosols may play an important role in chlorine activation in winter polar stratosphere, via heterogeneous processes similar to those occurring on PSC surfaces. The mechanism for heterogeneous reactions is identified.

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DEDICATION

This thesis is dedicated to my wife, Song Li, for her love, patience, and encouragement.
Table of Contents

Title Page .................................................................................................................. 1
Abstract ..................................................................................................................... 2
Acknowledgements ................................................................................................. 4
Curriculum Vita ....................................................................................................... 5
Dedication ................................................................................................................. 8
Table of Contents ................................................................................................... 9
List of Figures ......................................................................................................... 14
List of Tables .......................................................................................................... 27

1 Introduction ......................................................................................................... 30
  1.1 Background .................................................................................................... 30
  1.2 Outline of the Thesis .................................................................................... 35

2 Current Status of Polar Stratospheric Clouds (PSCs) and
  Heterogeneous Chemistry for Ozone Depletion ................................................. 37
  2.1 Characteristics of PSCs .............................................................................. 37
  2.2 Characteristics of Background Stratospheric Sulfate Aerosols ................. 43
  2.3 Laboratory Measurements ........................................................................... 46

3 Physical Chemistry of Two-Component Acid Systems and
  Stratospheric Implications .................................................................................. 50
  3.1 Background .................................................................................................. 51
    3.1.1 The phase role ..................................................................................... 51
3.1.2 The Gibbs-Duhem relation ............................................. 53

3.2 Experimental ........................................................................ 54

3.2.1 Vapor Pressure Measurements ....................................... 54

3.2.2 Calorimetric and Conductivity Measurements ............... 57

Differential Scanning Calorimetry (DSC) .............................. 57

Differential Thermal Analysis (DTA) ..................................... 59

Electrical Conductance .......................................................... 64

3.2.3 Infrared Spectroscopic Measurements ......................... 64

3.2.4 Sample Preparation and Supercooling Information .......... 66

3.3 The H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O Binary System .............. 67

3.3.1 Introduction ................................................................. 67

3.3.2 Vapor Pressures ............................................................ 68

Liquid and Supercooled Liquid .............................................. 68

Freezing Envelopes ............................................................. 77

Solids .................................................................................... 80

Melting Sulfuric Acid Tetrahydrate ........................................ 84

3.3.3 Infrared Spectra ............................................................ 85

Liquid and supercooled liquid .............................................. 85

Crystalline Sulfuric Acid Hydrates ........................................ 85

3.3.4 Calorimetric Measurements ........................................... 92

3.3.5 Freezing, Supercooling, and Glass Transition Temperatures 95

3.3.6 Stratospheric Implications ............................................ 97
3.4 The HCl/H₂O Binary System ...................................................... 100
3.4.1 Introduction ................................................................. 100
3.4.2 Thermal Analysis and Electrical Conductivity .................. 102
3.4.3 Vapor Pressures ............................................................. 107

3.5 The HNO₃/H₂O Binary System .................................................. 110
3.5.1 Introduction ................................................................. 110
3.5.2 Thermal Analysis ............................................................. 111

3.6 Thermodynamics and Phase Equilibria for the Binary Acid Systems:

Theoretical Considerations ..................................................... 116
3.6.1 Introduction ................................................................. 116
3.6.2 Methodology ................................................................. 116
3.6.3 The HNO₃/H₂O Binary System ............................................ 120
3.6.4 The HCl/H₂O Binary System ............................................. 122
3.6.5 The H₂SO₄/H₂O Binary System .......................................... 122

4 Physical Chemistry of Multi-Component Acid Systems of

Stratospheric Importance ....................................................... 131
4.1 Introduction ........................................................................... 132
4.2 Liquid H₂SO₄/HNO₃/H₂O and H₂SO₄/HNO₃/H₂O Ternary Systems ........ 134
4.2.1 Experimental .................................................................... 134
4.2.2 Vapor Pressure Results .................................................... 135

The H₂SO₄/HNO₃/H₂O Ternary System ........................................ 135
The H₂SO₄/HCl/H₂O Ternary System .......................................... 141

11
4.2.3 Henry's Law Solubility Constants ........................................ 144
  The $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ Ternary System .................. 144
  The $\text{H}_2\text{SO}_4/\text{HCl/}\text{H}_2\text{O}$ Ternary System .................. 158

4.2.4 Equilibrium Compositions of the Supercooled Stratospheric Aerosols .................................................. 164

4.3 Liquid $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl/}\text{H}_2\text{O}$ Quaternary System .................... 170
  4.3.1 Vapor Pressures .................................................. 170
  4.3.2 HCl Henry's Law Solubility Constants ............................ 171
  4.3.3 Equilibrium HCl Concentration in Supercooled Stratospheric Aerosols at Low Temperatures ......................... 171

4.4 Crystallized $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ Ternary Solutions .................... 179
  4.4.1 Vapor Pressures .................................................. 181
  4.4.2 The Mechanism for Polar Stratospheric Cloud Formation .... 194

5. Heterogeneous Interactions of $\text{ClONO}_2$ and HCl on Surfaces of

  Proposed PSC Materials .................................................. 198

  5.1 Introduction .................................................. 199

  5.2 Experimental .................................................. 202
    5.2.1 The Molecular Beam Mass Spectrometer (MBMS) System ...... 202
    5.2.2 The Flow Tube .................................................. 207
    5.2.3 Reactant and Gas Sources ...................................... 209
    5.2.4 Calibrations of the MBMS System .............................. 210

  5.3 Heterogeneous Interactions of $\text{ClONO}_2$ and HCl with
Sulfuric Acid Tetrahydrate (SAT).......................................................... 214

5.3.1 RESULTS ................................................................................. 214
   HCl Uptake Experiments ............................................................... 215
   Reaction of ClONO₂ with H₂O ...................................................... 222
   Reaction of ClONO₂ with HCl ...................................................... 230

5.3.2 Discussion .............................................................................. 231
   HCl Uptake Experiments ............................................................... 231
   Reaction of ClONO₂ with H₂O ...................................................... 239
   Reaction of ClONO₂ with HCl ...................................................... 240

5.3.3 Stratospheric Implications ...................................................... 241

5.4 Mechanism of the Heterogeneous Reactions .......................... 242

6 Conclusions .................................................................................. 253

References ...................................................................................... 256
List of Figures

Figure 2.1  Particle volume as a function of ambient temperature measured by FSSP during the AASE campaign. After Dye et al. [1992]. (42)

Figure 3.1  HNO₃ vs. H₂O vapor pressures for the HNO₃/H₂O binary system. The dashed lines are isotherms, and the solid lines represent coexistence conditions for two condensed phases. After Worsnop et al. [1993]. (52)

Figure 3.2  Schematic diagram of the experimental apparatus employed in the vapor pressure measurements. (55)

Figure 3.3  Schematic representation of the two principal thermal analysis systems. (58)

Figure 3.4  An example of DSC run for cooling a pure water and subsequent warming. The cooling rate is 4°C/min, and the warming rate is 10°C/min (the larger heating rate is necessary to increase sensitivity; it causes the ice-melting peaks to appear at a higher temperature). (60)

Figure 3.5  DTA warming curves for two HCl solutions of 10 and 15 wt %. The peaks near -74°C correspond to the ice/hexahydrate eutectic, whereas the peaks at warmer temperatures represent melting of ice. (61)

Figure 3.6  Schematic diagram of the experimental apparatus employed in the electrical
conductivity measurements. (62)

Figure 3.7 Conductance variation with temperature when cooling a 0.1 wt % HCl solution and warming. (63)

Figure 3.8 Schematic diagram of the cell used for infrared transmission measurements. (65)

Figure 3.9 Water vapor pressures of liquid and supercooled liquid. Weight percentages of H$_2$SO$_4$ are labeled in the figure. The solid lines are the least squares fits of the experimental data (open circles) from this work. The dashed-dotted lines are data taken from Jaecker-Voirol et al. [1990a, b], and the dashed lines from Gmitro and Vermeulen [1964]. (70)

Figure 3.10 Water vapor pressures as a function of H$_2$SO$_4$ wt % at 200 and 250 K. The solid lines are results from this study, while the dashed lines are calculated using the tabulated relative chemical potentials reported by Zeleznik [1991]. (72)

Figure 3.11 Sulfuric acid vapor pressures calculated from the Gibbs-Duhem equation (solid lines). The data from Jaecker-Voirol et al. [1990a, b] are plotted as long dashed lines for comparison. (76)

Figure 3.12 Water vapor pressures over partially frozen mixtures. The open circles and solid line are results from this study, while the dotted line is the intersections of the Jaecker-Voirol et al. [1990a, b] vapor pressure data with the freezing points reported by Gable et al. [1950]. The ice line is also plotted for reference. (78)

Figure 3.13 Sulfuric acid vapor pressures over partially frozen mixtures calculated from the Gibbs-Duhem equation and the freezing points reported by Gable et al. [1950] (solid curve). The dashed curve is obtained using the Jaecker-Voirol et al. [1990a,
b) vapor pressure data.

Figure 3.14  Vapor pressures of water for solids in the H$_2$SO$_4$/H$_2$O binary system: +, tetrahydrate/dihydrate; □, ice/tetrahydrate or ice/octahydrate; \( \nabla \), ice/hemihexahydrate. The coexistence lines and the freezing envelopes are labeled. The dashed lines are for H$_2$O vapor pressures of liquid solutions. The solid line F-C-M represent a warming process at a H$_2$O partial pressure of 3.8x10$^{-4}$ Torr (corresponding to a mixing ratio of 5 ppmv at 100 mb, ~16 km altitude in the stratosphere). Point Q labels the quadruple point for H$_2$SO$_4$•2H$_2$O and H$_2$SO$_4$•4H$_2$O coexisting with the gas and the liquid phases.

Figure 3.15  Infrared spectra of liquid H$_2$SO$_4$ solutions with compositions of 39, 43, 58, 65, and 73 wt % at temperatures near 300 and 190 K.

Figure 3.16  Spectra of crystalline hydrates H$_2$SO$_4$•nH$_2$O. For $n = 1$, 2, and 3 the spectra are presented at low temperatures (~ 140 K), showing sharper absorption bands. Spectra for $n = 4$, 6.5, and 8 change relatively little with temperature and are shown at 195 K.

Figure 3.17  Evolution of infrared spectra of a 47.6 wt % H$_2$SO$_4$ solutions with temperatures. Crystallization of H$_2$SO$_4$•6.5H$_2$O occurs between 190 and 200 K upon cooling. No significant changes occur upon warming to 210 K. The hemihexahydrate converts into tetrahydrate plus liquid at around 220 K. The tetrahydrate melts by 233 K.

Figure 3.18  DSC warming curves showing hydrate meltings. The peaks near 200 K represent either the eutectic meltings of ice/tetrahydrate followed by crystallization into hemihexahydrate, or the solid to solid conversion of octahydrate into hemihexahydrate. The coexistence mixtures of ice/hemihexahydrate melt near 211
K. For the 50 wt % \( \text{H}_2\text{SO}_4 \) frozen mixture, the \( \text{H}_2\text{SO}_4 \cdot 6.5\text{H}_2\text{O} \) undergoes a peritectic reaction at 219 K to form \( \text{H}_2\text{SO}_4 \cdot 4\text{H}_2\text{O} \). For the 20 wt % \( \text{H}_2\text{SO}_4 \) frozen mixture, the warmest peak corresponds the melting of ice. Weight percentages of \( \text{H}_2\text{SO}_4 \) are labeled in the figure.

Figure 3.19 Additional DSC cooling and warming curves of various \( \text{H}_2\text{SO}_4 \) solutions.

Figure 3.20 Equilibrium sulfuric acid compositions of background stratospheric aerosols as a function of temperature and \( \text{H}_2\text{O} \) mixing ratios at 100 mb (~16 km altitude), as estimated from different vapor pressure data: the solid lines are based on data from this work (\( \text{a} \), 5 ppmv; \( \text{b} \), 3 ppmv \( \text{H}_2\text{O} \)); the dashed line is based on data of Jaeckel-Voirol et al. [1990a, b] (5 ppmv \( \text{H}_2\text{O} \)); the dashed-dotted line is from the results of Steele et al. [1983] (5 ppmv \( \text{H}_2\text{O} \)). Also shown in this figure is the freezing envelop of sulfuric acid solutions [Gable et al., 1950]. Points \( F \) and \( M \) label the corresponding freezing and melting points.

Figure 3.21 DSC warming curves of various HCl solutions. The negative peaks around -80°C indicate crystallization, which is accompanied by a heat release. The peaks near -70°C correspond to melting of HCl hexahydrate, and the peaks above -20°C represent melting of the HCl-doped ice, which is absent for the 25 wt % solution. The heating rates are 4°C/min for the 25 and the 11 wt % solution, and 10°C/min for the 2 wt % solution.

Figure 3.22 DSC warming curves for 23 and 26.6 wt % HCl solutions.

Figure 3.23 HCl vapor pressures of the HCl/\( \text{H}_2\text{O} \) binary system: \( \Delta \), liquid/solid; \( + \), ice/hexahydrate. The long dashed lines are vapor pressures of liquid HCl solutions extrapolated from the data of Fritz and Fuget [1956]. The tri/hexahydrate coexistence line is taken from the data of Hanson and Mauersberger [1990]. The
short dashed lines are the freezing envelope. \hspace{1cm} (108)

Figure 3.24 DSC cooling and warming curves of various HNO$_3$ solutions. The 53.4 and 63.4 wt % solutions correspond to the NAT and NAD compositions, whereas the 32.5 and 70 wt % solutions correspond to the ice/NAT and NAT/NAM eutectic mixtures. \hspace{1cm} (112)

Figure 3.25 Evolution of infrared spectra with temperature for a frozen 63.4 wt % HNO$_3$ solution. \hspace{1cm} (113)

Figure 3.26 Heat capacity of the HNO$_3$/H$_2$O binary system. \hspace{1cm} (128)

Figure 3.27 Same as Figure 3.23 except for the dotted line, which is determined using equation (3.25) and the liquid HCl vapor pressure data of Fritz and Fuget [1956] at the ice/hexahydrate eutectic. \hspace{1cm} (129)

Figure 3.28 Same as Figure 3.14 except for the dotted line, which is determined using equation (3.24) and our measured liquid H$_2$O vapor pressure at the di-/tetrahydrate eutectic. \hspace{1cm} (130)

Figure 4.1 (a) Nitric acid and (b) water vapor pressures over aqueous H$_2$SO$_4$/HNO$_3$/H$_2$O solutions for 35 % wt sulfuric acid of various nitric acid contents. Weight percents of nitric acid are indicated in the figure. The solid lines are fits to the experimental data. The dashed-dotted lines are calculated HNO$_3$ vapor pressures according to Jaecker-Voirol et al.[1990a, b]. The dashed line represents H$_2$O vapor pressures for zero nitric acid, discussed in section 3.3.2. \hspace{1cm} (136)

Figure 4.2 Same as Figure 4.1 except for 40 % wt sulfuric acid. \hspace{1cm} (137)

Figure 4.3 Same as Figure 4.1 except for 50 % wt sulfuric acid. \hspace{1cm} (138)
Figure 4.4 HCl vapor pressures over aqueous $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$ solutions for 0.1 % wt HCl of various $\text{H}_2\text{SO}_4$ contents. (142)

Figure 4.5 The HCl signal as a function of time over a 60 wt % $\text{H}_2\text{SO}_4$ and 0.1 wt % HCl solution at 210 K, demonstrating the effect of HCl surface depletion. The sample was initially stirred for 0.7 min, before sampling the vapors with the mass spectrometer. (143)

Figure 4.6 Nitric acid vapor pressure vs. nitric acid molarity for 35-75 % wt sulfuric acid solutions at 220 K. (147)

Figure 4.7 Temperature dependence of the effective Henry's law constants for $\text{HNO}_3$ in 40-75 % wt sulfuric acid. The dashed-dotted lines are results for 58 % and 74 % sulfuric acid reported by Reihs et al. [1990]. The value at 283 K (▽) is for 73% sulfuric acid from the work of Van Doren et al. [1991]. The two solid circles (●) are values for 60 and 75 % wt $\text{H}_2\text{SO}_4$ estimated from the data of Vandoni [1944]. (149)

Figure 4.8 Enthalpies of condensation of $\text{HNO}_3$ for the aqueous $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ternary system. (153)

Figure 4.9 Temperature dependence of the effective Henry's law constants for HCl in 35-60 % wt sulfuric acid. The dotted line is based on our measurements for a 60 wt % $\text{H}_2\text{SO}_4$ solution without stirring, and the long dashed lines are from Hanson and Ravishankara [1993]. The value at 222 K (open triangle) is for a 60% sulfuric acid from the work of Williams and Golden [1993]. (159)

Figure 4.10 Enthalpies of condensation of HCl for the aqueous HCl/$\text{H}_2\text{SO}_4/$H$_2$O ternary system. (161)
Figure 4.11  Equilibrium sulfuric acid composition of background stratospheric aerosols as a function of temperature and ambient mixing ratios of water and nitric acid at 100 mb (5 ppmv H$_2$O and 5 ppbv or 10 ppbv HNO$_3$, ~16 km altitude). The dashed-dotted curve is for the case of zero nitric acid, discussed in section 3.3.2. Also shown in this figure is the freezing envelop of sulfuric acid solutions. The top axis labels the H$_2$SO$_4$ mole fraction for the H$_2$SO$_4$/H$_2$O binary system.  

Figure 4.12  Equilibrium nitric acid composition of background stratospheric aerosols as a function of temperature and ambient mixing ratios of water and nitric acid at 100 mb (5 ppmv H$_2$O and 5 ppbv or 10 ppbv HNO$_3$, ~16 km altitude). The top axis labels the HNO$_3$ mole fraction in the HNO$_3$/H$_2$SO$_4$/H$_2$O ternary system.  

Figure 4.13  HCl vapor pressures over various HCl/HNO$_3$/H$_2$SO$_4$/H$_2$O quaternary solutions: (a) 25 wt % H$_2$SO$_4$ and 20 wt % HNO$_3$; (b) 30 wt % H$_2$SO$_4$ and 15 wt % HNO$_3$; (c) 35 wt % H$_2$SO$_4$ and 10 wt % HNO$_3$; (d) 40 wt % H$_2$SO$_4$ and 5 wt % HNO$_3$. For all the solutions the HCl concentration is 0.1 wt %.  

Figure 4.14  Temperature dependence of the effective Henry’s law constants of HCl in the HCl/HNO$_3$/H$_2$SO$_4$/H$_2$O quaternary solutions: (a) 25 wt % H$_2$SO$_4$ and 20 wt % HNO$_3$; (b) 30 wt % H$_2$SO$_4$ and 15 wt % HNO$_3$; (c) 35 wt % H$_2$SO$_4$ and 10 wt % HNO$_3$; (d) 40 wt % H$_2$SO$_4$ and 5 wt % HNO$_3$. For all the solutions the HCl concentration is 0.1 wt %.  

Figure 4.15  HCl solubility constant as a function of stratospheric temperature. The three sets of curves correspond to 10 ppbv HNO$_3$ and to 5, 3, and 2 ppmv H$_2$O at 100 mb, respectively. The solid curves represent HCl solubility in the HNO$_3$/H$_2$SO$_4$/H$_2$O ternary aerosols, whereas the dashed curves represent the HCl solubility in the H$_2$SO$_4$/H$_2$O binary aerosols.  

Figure 4.16  Time evolution of mass spectrometer signals for H$_2$O ($m/e$ 18) and HNO$_3$ ($m/e$ 46).
46) before and after addition of gaseous HNO$_3$ to a frozen solution consisting of 10 % wt HNO$_3$ and 50 % wt H$_2$SO$_4$ at 210 K. (183)

Figure 4.17  Equilibrium vapor pressures of HNO$_3$ plotted against H$_2$O for a frozen solution containing 10 % wt HNO$_3$ and 50 % wt H$_2$SO$_4$ in the liquid phase. The dotted lines denote phase boundaries between ice, HNO$_3$$\cdot$3H$_2$O, and HNO$_3$$\cdot$H$_2$O as well as between the solid and liquid phases [Hanson and Mauersberger, 1988a]. The solid curve delineates the liquid-solid phase boundary of H$_2$SO$_4$$\cdot$4H$_2$O, with the HNO$_3$ vapor pressure determined from the temperature and H$_2$O vapor pressure of H$_2$SO$_4$ freezing envelope and from the Gibbs-Duhem relation (Equation (3.3)). (184)

Figure 4.18  Equilibrium H$_2$O vapor pressures from the data in Figure 4.17. The dotted-dashed lines represent phase boundaries between ice, H$_2$SO$_4$$\cdot$6.5H$_2$O, H$_2$SO$_4$$\cdot$4H$_2$O, and H$_2$SO$_4$$\cdot$2H$_2$O as well as between the solid and liquid phases. The dotted line corresponds to H$_2$O vapor pressures of the coexistence of HNO$_3$$\cdot$3H$_2$O and HNO$_3$$\cdot$H$_2$O [Hanson and Mauersberger, 1988a]. (185)

Figure 4.19  Temperature evolution of the equilibrium vapor pressures of HNO$_3$ and H$_2$O over a previously frozen solution containing 12 % wt HNO$_3$ and 38 % wt H$_2$SO$_4$ in the liquid phase, with symbols as in Figure 4.17. (189)

Figure 4.20  Infrared spectra of various crystallized H$_2$SO$_4$/HNO$_3$/H$_2$O solutions. The spectra of pure NAT, SAT, and SAH are shown in the figure for comparison. The numbers correspond to those given in Table 4.10. (190)

Figure 4.21  DSC warming curves showing melting of crystallized H$_2$SO$_4$/HNO$_3$/H$_2$O samples. Also shown for comparison as the two upper traces are the warming curves of 20 and 50 wt % H$_2$SO$_4$ solutions. For the sample with 38.7 wt % H$_2$SO$_4$ and 9.3 wt % HNO$_3$ the solid-solid phase transition temperatures match closely those of the
H$_2$SO$_4$/H$_2$O binary system: the peaks (a) near 200 K represent either the eutectic melting of ice/H$_2$SO$_4$ tetrahydrate (SAT) followed by crystallization into H$_2$SO$_4$ hemihexahydrate (SAH), or the solid-solid conversion of octahydrate into SAH; the coexistence mixture of ice/SAH has an eutectic near 211 K (peak b), which is little changed in the ternary eutectic; and the peritectic transformation of SAH to SAT occurs at 219 K (peak c), which is again essentially the same in the binary and ternary systems. The two small peaks (e and f) correspond to the melting of SAT at 230 K and NAT at 233 K, respectively. For the sample with 50 wt % H$_2$SO$_4$ and 10 wt % HNO$_3$ the peak (d) at 220 K most likely represents the eutectic melting of NAT and SAT, which is followed by the melting of SAT near 240 K (peak g).

Figure 4.22  Ternary diagram for the H$_2$SO$_4$/HNO$_3$/H$_2$O system. Superimposed upon this figure are the dilution curves (solid lines) for liquid stratospheric aerosols at 100 mb (~16 km) and at ambient mixing ratios of 5 ppmv H$_2$O; and 10 ppbv HNO$_3$ (a), 5 ppbv HNO$_3$ (b), and 2.5 ppbv HNO$_3$ (c). Also shown along the dilution lines are the equilibrium temperatures (dotted lines), the frost point of crystalline HNO$_3$$\cdot$3H$_2$O (i.e., $S_{\text{NAT}} = 1$) (●), and the point at which the HNO$_3$ vapor pressure reaches a supersaturation of 10 with respect to NAT ($S_{\text{NAT}} = 10$) (■). The temperatures and compositions of the dilution curves are calculated from our H$_2$SO$_4$/HNO$_3$/H$_2$O vapor pressure data and extrapolated below ~195 K to the intercepts on the HNO$_3$/H$_2$O line estimated with the vapor pressure data of Hanson [1990]. For case (~ the HNO$_3$/H$_2$O line is reached at 193.5 K; the ice frost point is 192.6 K for 5 ppmv H$_2$O at 100 mb. The dashed curves are the eutectic lines reported by Carpenter and Lehrman [1925]; also indicated is the identity of the various solids that at equilibrium crystallize first upon cooling liquids with compositions bounded by the eutectic lines.

Figure 5.1  Schematic diagram of the experimental apparatus used to study the heterogeneous
reactions on proposed PSC materials.  

Figure 5.2 Flux of molecules through the 1 mm diameter pin-hole as a function of gas density in the first stage chamber evacuated by the 10" diffusion pump. Slope of the line is an empirical determination of the pumping speed of the diffusion pump and is $10^4$ L/s.

Figure 5.3 Sensitivity test of the MBMS system using SF$_6$ as an inert tracer species. The total pressures in the flow tube are labeled in this figure.

Figure 5.4 H$_2$O calibration over the temperature range of 230 to 200 K. The slope of the line yields the enthalpy of sublimation of ice and is 50.24 kJ/mole.

Figure 5.5 Calibration of HNO$_3$ over the partial pressure range of $5\times10^{-7}$ to $5\times10^{-6}$ Torr.

Figure 5.6 HNO$_3$ vs. H$_2$O vapor pressures for an NAT film prepared at 220 K in the flow tube, verifying the H$_2$O and HNO$_3$ calibrations. The solid line is the 220 K isotherm for NAT from Hanson and Mauersberger [1988a].

Figure 5.7 Time evolution of the HCl signal for two typical HCl uptake experiments on SAT at 195 K and $P_{\text{H}_2\text{O}} = 4\times10^{-4}$ torr: (top trace) $P_{\text{HCl}} = 6.7\times10^{-7}$ torr, and (bottom trace) $P_{\text{HCl}} = 2\times10^{-5}$ torr. The injector is pulled upstream by 5 cm at 1 min, and returned to its original position at 3 min.

Figure 5.8 HCl surface coverages on SAT films as a function of $P_{\text{HCl}}$ at 195 K and $P_{\text{H}_2\text{O}} = 4.5\times10^{-4}$ torr. The solid curve is a fit of the experimental data in the form of equation (5.6) and is also summarized in Table 5.1.
Figure 5.9  HCl surface coverages on SAT films as a function of $P_{H_2O}$ at 195 K and $P_{HCl} \approx 5 \times 10^{-7}$ torr. Also shown in this figure is the result of HCl uptakes measured on fresh ice films (open triangle, average of 9 experiments). The ice vapor pressure at this temperature is labeled. The solid curve is a fit of the experimental data in the form of equation (5.6) and is also summarized in Table 5.1.  

(219)

Figure 5.10  HCl surface coverages on SAT films as a function of temperature at $P_{H_2O} = 3.4 \times 10^{-4}$ torr and $P_{HCl} \approx 6 \times 10^{-7}$ torr. The ice frost point is labeled. The solid curve is a fit of the experimental data in the form of equation (5.6) and is also summarized in Table 5.1.  

(220)

Figure 5.11  Time evolution of ClONO$_2$ ($m/e = 46$) and HOCl ($m/e = 52$) signals for a typical ClONO$_2$ reactive uptake experiment on SAT. Experimental conditions: $P_{ClONO_2} = 7 \times 10^{-8}$ torr, $P_{H_2O} = 4 \times 10^{-4}$ torr, $P_{He} = 0.8$ torr, velocity = 1371 cm s$^{-1}$, and $T = 195$ K.  

(225)

Figure 5.12  ClONO$_2$ (top trace) and HOCl (bottom trace) signals as a function of injector position. For the HOCl growth curve the first-order rate constant is calculated from the slope of a plot $(S_{HOCl}(\infty) - S_{HOCl}(z))$ (solid curve), where $S_{HOCl}(z)$ and $S_{HOCl}(\infty)$ are the HOCl signal at infinite reaction time (see text for details). Experimental conditions: $P_{ClONO_2} = 7 \times 10^{-8}$ torr, $P_{H_2O} = 5.4 \times 10^{-4}$ torr, $P_{He} = 1.0$ torr, velocity = 1500 cm s$^{-1}$, and $T = 195$ K.  

(226)

Figure 5.13  Reaction probability ($\gamma_1$) for reaction (5.1) as a function of $P_{H_2O}$ on SAT surfaces at 195 K. Open circles are $\gamma_1$'s determined by ClONO$_2$ decay, and solid circles are determined by HOCl growth. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.2. Also shown in this figure are $\gamma_1$'s measured on fresh ice films (open square, average of 15 experiments) and on HNO$_3$-treated ice films (solid square, average

24
of 11 experiments). The ice vapor pressure at this temperature is labeled. Experimental conditions: $P_{\text{ClONO}_2} = 3 \times 10^{-8} \rightarrow 5 \times 10^{-8}$ torr, $P_{\text{He}} = 0.9 \rightarrow 1.0$ torr, velocity $= 1300 \rightarrow 1500$ cm s$^{-1}$, and $T = 195$ K. \hspace{1cm} (227)

Figure 5.14 Reaction probability ($\gamma_1$) for reaction (5.1) as a function of temperature on SAT surfaces. Open circles are $\gamma_1$'s determined by ClONO$_2$ decay, and solid circles are determined by HOCl growth. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.2. The ice frost point is labeled. Experimental conditions: $P_{\text{ClONO}_2} = 2 \times 10^{-8} \rightarrow 4 \times 10^{-8}$ torr, $P_{\text{H}_2\text{O}} = 3.4 \times 10^{-4}$ torr, $P_{\text{He}} = 0.9 \rightarrow 1.0$ torr, velocity $= 1300 \rightarrow 1600$ cm s$^{-1}$, and $T = 195$ K. \hspace{1cm} (228)

Figure 5.15 Time evolution of ClONO$_2$ ($m/e = 46$) and Cl$_2$ ($m/e = 70$) signals for a typical ClONO$_2$ reactive uptake experiment on SAT in the presence of HCl vapor. Experimental conditions: $P_{\text{ClONO}_2} = 7 \times 10^{-8}$ torr, $P_{\text{H}_2\text{O}} = 4 \times 10^{-4}$ torr, $P_{\text{HCl}} = 4 \times 10^{-7}$ torr, $P_{\text{He}} = 1.3$ torr, velocity $= 1400$ cm s$^{-1}$, and $T = 195$ K. \hspace{1cm} (232)

Figure 5.16 ClONO$_2$ (top trace) and Cl$_2$ (bottom trace) signals as a function of injector position. For the Cl$_2$ growth curve the first-order rate constant is calculated from the slope of a plot ($S_{\text{Cl}_2}(\infty) - S_{\text{Cl}_2}(z)$) (solid curve), where $S_{\text{Cl}_2}(\infty)$ is the Cl$_2$ signal at infinite reaction time (see text for details). Experimental conditions: $P_{\text{ClONO}_2} = 7 \times 10^{-8}$ torr, $P_{\text{H}_2\text{O}} = 2.4 \times 10^{-4}$ torr, $P_{\text{HCl}} = 5 \times 10^{-7}$ torr, $P_{\text{He}} = 1.0$ torr, velocity $= 1571$ cm s$^{-1}$, and $T = 195$ K. \hspace{1cm} (233)

Figure 5.17 Reaction probability ($\gamma_2$) for reaction (5.2) as a function of $P_{\text{H}_2\text{O}}$ on SAT surfaces at 195 K. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.3. Open circles are $\gamma_2$'s determined by ClONO$_2$ decay, and solid circles are determined by Cl$_2$ growth. The ice vapor pressure at this temperature is labeled. Experimental
conditions: \( P_{\text{ClONO}_2} = 3 \times 10^{-8} \rightarrow 5 \times 10^{-8} \text{ torr} \), \( P_{\text{HCl}} = 4 \times 10^{-7} \rightarrow 8 \times 10^{-7} \text{ torr} \), \( P_{\text{He}} = 0.9 \rightarrow 1.0 \text{ torr} \), velocity = 1300 \( \rightarrow \) 1600 cm s\(^{-1} \), and \( T = 195 \text{ K} \). \hspace{1cm} (234)

Figure 5.18 Reaction probability \( (\gamma_2) \) for reaction (5.2) as a function of temperature on SAT surfaces. Open circles are \( \gamma_2 \)'s determined by ClONO\(_2\) decay, and solid circles are determined by HOCl growth. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.3. The ice frost point is labeled. Experimental conditions: \( P_{\text{ClONO}_2} = 3 \times 10^{-8} \rightarrow 5 \times 10^{-8} \text{ torr} \), \( P_{\text{H}_2\text{O}} = 5.6 \times 10^{-4} \text{ torr} \), \( P_{\text{HCl}} = 4 \times 10^{-7} \rightarrow 8 \times 10^{-7} \text{ torr} \), \( P_{\text{He}} = 0.9 \rightarrow 1.0 \text{ torr} \), velocity = 1300 \( \rightarrow \) 1600 cm s\(^{-1} \), and \( T = 195 \text{ K} \). \hspace{1cm} (235)

Figure 5.19 Mass Spectra of the DCl bubbler effluent before exposure to a solid film. \hspace{1cm} (249)

Figure 5.20 Interaction of DCl with \( \text{H}_2\text{O} \) on an ice film at 195 K: at 0.8 min, a 5-cm length of the ice film is exposed to DCl by pulling the injector upstream; at 5 min, the injector is moved back to its original position to stop the exposure. Both HCl and DCl signals return to their initial concentrations upon pushing back the injector. \hspace{1cm} (250)

Figure 5.21 Interaction of DCl with \( \text{H}_2\text{O} \) on \( \text{H}_2\text{SO}_4 \)-rich SAT with a \( \text{H}_2\text{O} \) partial pressure of 1.7\( \times \)10\(^{-4} \) Torr at 195 K (corresponding to 30% relative humidity). \hspace{1cm} (251)

Figure 5.22 Conductance variation with temperature for an HCl-doped power ice sample. The sample appeared dry and visually showed no sign of melting after being exposed to HCl vapor. The drop in the electrical conductivity upon warming to 173 K suggests that HCl migrates into the bulk to form a distinct \( \text{H}_2\text{O}-\text{HCl} \) phase in the form of HCl•6H\(_2\text{O} \), as evident by the melting temperature at 198 K, corresponding to the ice/hexahydrate eutectic, discussed in section 3.4.3. \hspace{1cm} (252)
List of Tables

TABLE 2.1 Polar stratospheric cloud particles and stratospheric background sulfate aerosols. (41)

TABLE 2.2 Reaction probabilities involving HCl on PSC surfaces. (48)

TABLE 2.3 Reaction probabilities for the hydrolysis of ClONO$_2$ and N$_2$O$_5$ on PSC surfaces. (49)

TABLE 3.1 Coefficients from a least-squares fit of log $P_w = A - B/T$ for water vapor pressures in the H$_2$SO$_4$/H$_2$O binary system. (69)

TABLE 3.2 Values of the coefficients for equation (3.4). (74)

TABLE 3.3 Values of the coefficients to be used in equation (3.5). (75)

TABLE 3.4 Frequencies (cm$^{-1}$) of major infrared bands of crystalline hydrates of H$_2$SO$_4$ sampled at 143 ± 10 K. (89)

TABLE 3.5 Enthalpies of fusion of HCl hydrates. (106)

TABLE 3.6 Enthalpies of fusion of nitric acid hydrates. (114)
TABLE 3.7 Thermodynamic data for components at the standard state. (124)

TABLE 3.8 Enthalpies of the binary systems. (125)

TABLE 3.9 Entropies of the binary systems. (126)

TABLE 3.10 Coexistence line slopes at 200 K. (127)

TABLE 4.1 Coefficients $A$ and $B$ from a least-squares fit of $\log P = A - B/T$ for HNO$_3$ vapor pressures in the HNO$_3$/H$_2$O/H$_2$SO$_4$ ternary system. (139)

TABLE 4.2 Coefficients $A$ and $B$ from a least-squares fit of $\log P = A - B/T$ for H$_2$O vapor pressures in the HNO$_3$/H$_2$O/H$_2$SO$_4$ ternary system. (140)

TABLE 4.3 Effective Henry's law constants $H^*$ for the H$_2$SO$_4$/HNO$_3$/H$_2$O ternary system: coefficients $A$ and $B$ for the equation $\ln H^* = A + B/T$. (150)

TABLE 4.4 Parameters to be used in equation (4.11) for estimating HNO$_3$ vapor pressures in the HNO$_3$/H$_2$SO$_4$/H$_2$O ternary system. (156)

TABLE 4.5 Parameters to be used in equation (4.12) for estimating H$_2$O vapor pressures in the HNO$_3$/H$_2$SO$_4$/H$_2$O ternary system. (157)

TABLE 4.6 Effective Henry's law constants $H^*$ for the H$_2$SO$_4$/HCl/H$_2$O ternary system: coefficients $A$ and $B$ for the equation $\ln H^* = A + B/T$. (160)

TABLE 4.7 Coefficients $A$ and $B$ from a least-squares fit of $\log P = A - B/T$ for HCl vapor pressures in the H$_2$SO$_4$/HNO$_3$/HCl/H$_2$O quaternary system. (174)
TABLE 4.8  Effective Henry’s law constants $H^*$ for the H$_2$SO$_4$/HNO$_3$/HCl/H$_2$O quaternary system: coefficients $A$ and $B$ for the equation $\ln H^* = A + B/T$. \hspace{1cm} (176)

TABLE 4.9  Parameters to be used in equation (4.19) for estimating HCl solubility constants in the HNO$_3$/HCl/H$_2$SO$_4$/H$_2$O quaternary system. \hspace{1cm} (177)

TABLE 4.10  Spectral characteristics of the crystallized H$_2$SO$_4$/HNO$_3$/H$_2$O solutions along with the amounts that could separate into SAT, NAT, and ice by weight percent and information about spontaneous sample crystallization upon cooling to 190 K. \hspace{1cm} (193)

TABLE 5.1  Summary and parameterization of the HCl uptake experiments. \hspace{1cm} (221)

TABLE 5.2  Summary and parameterization of measurements for the heterogeneous reaction between ClONO$_2$ and H$_2$O. \hspace{1cm} (229)

TABLE 5.3  Summary and parameterization of measurements for the heterogeneous reaction between ClONO$_2$ and HCl. \hspace{1cm} (236)
Chapter 1

Introduction

1.1 Background

Atmospheric ozone, which absorbs much of the ultraviolet radiation from the sun, has long been recognized as an important atmospheric species. Changes in the total column content of ozone would modify the amount of biologically harmful ultraviolet radiation penetrating to the Earth’s surface with potential adverse effects on human beings and on the ecosystems. Changes in the vertical ozone distribution could also contribute the global climate change by modifying the atmospheric temperature structure.

Roughly 90% of the Earth’s ozone resides in the stratosphere. Ozone is generated in the stratosphere when solar ultraviolet radiation is absorbed by molecular oxygen, breaking the molecular bond and yielding two free oxygen atoms. A free oxygen atom can then combine with an oxygen molecule to form ozone. Ozone itself undergoes photodissociation as well as other loss
processes, yielding a net balance between ozone formation and ozone destruction. The temporal and spatial distributions of stratospheric ozone are controlled by the chemical, radiative, and dynamic processes, leading to a quasi-steady-state concentration of atmospheric ozone that is greatest in the lower stratosphere between about 15 and 30 km of altitude. The absorption of solar radiation in both the formation and the destruction of ozone heats the atmosphere, so that temperature increases with altitude form the tropopause up to about 50 km.

Over the past few decades, there have been highly significant advances in the understanding of the impact of human activities on the Earth’s stratospheric ozone layer. Anthropogenic sources, mainly chlorofluorocarbons (CFCs), have been shown to pose a threat to the ozone layer [Molina and Rowland, 1974]. CFCs, the widely-used industrial chemicals, are relatively inert in the troposphere and are mixed rapidly through the troposphere and gradually through stratosphere. Consequently, the photodissociation of CFCs could lead to a pronounced increase in the stratospheric chlorine content. The basic catalytic cycles responsible for most of the observed ozone loss are the ClO dimer mechanism [Molina and Molina, 1985],

\[
\text{ClO} + \text{ClO} + M \rightarrow (\text{ClO})_2 + M \quad (1.1)
\]

\[
(\text{ClO})_2 + h\nu \rightarrow \text{Cl} + \text{ClO} \quad (1.2)
\]

\[
\text{ClOO} + M \rightarrow \text{Cl} + \text{O}_2 + M \quad (1.3)
\]

\[
2(\text{Cl} + \text{O}_3) \rightarrow 2(\text{ClO} + \text{O}_2) \quad (1.4)
\]

\[
\text{Net: } 2\text{O}_3 \rightarrow 3\text{O}_2 \quad (1.5)
\]

and Br mechanism [McElroy et al., 1986a],

\[
\text{ClO} + \text{BrO} \rightarrow \text{Cl} + \text{Br} + \text{O}_2 \quad (1.6)
\]

\[
\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \quad (1.7)
\]
\[
\text{Br} + \text{O}_3 \rightarrow \text{BrO} + \text{O}_2 \\
\text{Net:} \ 2\text{O}_3 \rightarrow 3\text{O}_2
\] (1.8)

It is believed that at least 95% of the chemically catalyzed ozone loss in the polar stratosphere can be attributed to these chemical schemes: about 75% of the ozone loss results from reactions involving the ClO dimer, and most of the rest remaining ozone is destroyed in reactions involving bromine.

The discovery of the Antarctic Ozone hole [Farman et al., 1985] established that an unprecedented and completely unanticipated change in the total ozone column (by about 50%) had been observed in the Antarctic over the past decade, but only during the spring season. A change of this magnitude was not anticipated by model predictions, using the simple scenario of chlorine release by photodissociation of CFCs. The photodissociation of the CFCs is ordinarily followed by gas-phase reactions of gaseous chlorine monoxide with nitrogen dioxide, leading to the formation of chlorine nitrate, ClONO₂. In fact, most of the chlorine in the stratosphere should be bound up in the less reactive compounds ClONO₂ or HCl, referred to as reservoir species. Consequently, the models predicted that only a small fraction of the chlorine is present in reactive forms such as Cl or ClO.

Earlier satellite observations had shown that the Antarctic winter stratosphere is a region of extensive cloud formation [McCormick et al., 1982]. Recently, heterogeneous chemical reaction theory was advanced to explain that the Antarctic ozone hole depends critically on the persistence and characteristics of the PSCs. Solomon et al. [1986] and McElroy et al. [1986a] noted that the extreme cold temperatures of the Antarctic winter and spring shown by McCormick et al. [1982] might lead to greatly enhanced PSC occurrences. They suggested that
heterogeneous reactions such as

\[ \text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3 \]  \hspace{1cm} (1.10)

\[ \text{H}_2\text{O} + \text{ClONO}_2 \rightarrow \text{HOCl} + \text{HNO}_3 \]  \hspace{1cm} (1.11)

would both enhance the level of reactive chlorine at the expense of the reservoir species, HCl and ClONO\textsubscript{2} and suppress the abundance of reactive nitrogen (NO\textsubscript{x})\textsuperscript{1} in favor of the HNO\textsubscript{3} reservoir. The suppression of reactive nitrogen is particularly important, since it impedes the reformation of ClONO\textsubscript{2}, allowing the liberated reactive chlorine to remain active. Ozone depletion could then be expected to occur in the spring, when sunlight is available to rapidly photolyze Cl\textsubscript{2} and HOCl, driving the catalytic circles.

Seminal studies [Toon et al., 1986; Crutzen and Arnold, 1986; McElroy et al., 1986b] have advanced the explanation of the observed two PSC types. These results revealed that type I PSCs form above the frost point as HNO\textsubscript{3}/3H\textsubscript{2}O co-condenses on frozen background aerosol nuclei probably containing H\textsubscript{2}SO\textsubscript{4}, and that type II PSCs form subsequently below the frost point as H\textsubscript{2}O deposits on type I particles. The formation of type I PSCs would also suppress reactive gaseous nitrogen species (NO\textsubscript{x}), which counteract chlorine-catalyzed ozone destruction. Furthermore, as noted by Toon et al. [1986], such particles might remove reactive nitrogen irreversibly ("denitrify") from the polar stratosphere through sedimentation of large PSC particles containing HNO\textsubscript{3}.

Molina et al. [1987] have first experimentally showed that the reaction rates of (1.10) and (1.11) were greatly enhanced in the presence of ice particles. Their results supported that the PSCs foster the removal of halogen reservoir species and NO\textsubscript{x} from the gas phase by providing

\[ \text{NO}_x = \text{NO} + \text{NO}_2 \]
favorable surfaces. Reactions analogous to (1.10) and (1.11) were also studied by Tolbert et al. [1988] and Leu [1988a, b],

\[
\begin{align*}
N_2O_5 + HCl & \rightarrow ClNO_2 + HNO_3 \\
N_2O_5 + H_2O & \rightarrow 2HNO_3
\end{align*}
\]  \hspace{1cm} (1.12) \hspace{1cm} (1.13)

The extensive measurements of chemical changes obtained in the polar regions during recent years have firmly established a link between heterogeneous processing by PSCs and ozone loss. The observed increase in the reactive ClO and the concurrent decreases in HCl and ozone as measured from outside to inside of the chemically perturbed region over Antarctica and Arctic have provided further indication that the proposed heterogeneous reactions occurring on PSC particles are involved in the ozone loss [Anderson et al., 1989; Anderson et al., 1991; Brune et al., 1991; Webster et al., 1993].

In addition to the PSCs, there are also sulfate aerosols in the stratosphere, formed mainly by violent volcanic eruptions. At mid-latitudes, these aerosols are likely composed of 60 to 80 wt % H$_2$SO$_4$ solutions. Laboratory measurements have demonstrated that the heterogeneous reaction between N$_2$O$_5$ and H$_2$O proceeds readily on concentrated sulfuric solutions [Hanson and Ravishankara, 1991]. Model calculations have also indicated that the same reaction may account for a significant fraction of the larger-than-expected ozone trend on a global scale [Hofmann and Solomon, 1989].

Our understanding of physics and chemistry on PSCs and heterogeneous chemistry has improved greatly since the discovery of Antarctic ozone hole. Aircraft campaigns to Antarctica in 1987 (Airborne Antarctic Ozone Experiment, AAOE) and to the Arctic in 1989 and 1991 (Airborne Arctic Stratospheric Expedition, AASE I and II) have provided first-order answers
regarding processing of air by PSCs and microphysical and physical chemistry aspects of PSCs. Extensive laboratory experiments have also been carried out to study chemical reactivity on various proposed PSC materials and to predict phase properties and compositions of PSC particles as well as background stratospheric aerosols.

However, despite the recent efforts in understanding the process of stratospheric ozone depletion, many key questions still remain unresolved. For example, the mechanism of PSC formation as well the role of background sulfate aerosols in PSC nucleation remain unclear. The available knowledge still suffers from a lack of understanding on the nature and mechanism of the heterogeneous reactions at a fundamental, molecular level. Furthermore, while it is possible to parameterize the PSC formation and growth and the heterogeneous ozone depletion process in numerical models, such parameterization is severely hindered by the limited experimental information about the physical chemistry and chemical reactivity on proposed PSC materials.

This thesis was proposed and designated to tackle some of the questions. The main focus of this work is to investigate physical chemistry of binary as well as multi-component acid-water systems of stratospheric importance and to explore the mechanisms of PSCs formation and heterogeneous reactions, using various experimental methods.

1.2 Guide to the Thesis

Recent laboratory and field studies which discuss current state of PSCs and heterogeneous chemistry, with emphasis on phase properties and compositions of stratospheric particulate, are reviewed in Chapter 2. Chapter 3 presents laboratory investigations on the physical chemistry
of binary systems (i.e., H₂SO₄, HNO₃, and HCl) of stratospheric importance. The measurements include thermodynamic properties such as melting points, enthalpies of fusion, and vapor pressures and infrared spectra² of liquid and supercooled solutions, as well as of liquid-solid and solid-solid coexistence mixtures of those acid systems. A method for describing solid-solid phase equilibria in a binary system, based on chemical equilibrium principles, is also developed and compared with the experimental data for thermodynamic consistency.³ Chapter 4 addresses the issues of HCl and HNO₃ solubilities in H₂SO₄ solutions. The equilibrium HCl and HNO₃ compositions in stratospheric background aerosols are predicted as a function of temperature and HCl and HNO₃ partial pressures in the stratosphere. The mechanism of PSC formation is also investigated in this chapter. Heterogeneous interactions of ClONO₂ and HCl on sulfuric acid crystalline hydrates are discussed in Chapter 5. The surface chemistry and mechanism of the heterogeneous reactions on all proposed PSC materials are explored. Finally, a summary is given, along with concluding remarks, in Chapter 6.

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² The IR measurements were performed mainly by Dr. Paul Wooldridge, a postdoctoral fellow in the atmospheric chemistry research group; they are included in this thesis for the completeness, as the results are complementary to those carried out by the author.

³ The theoretical analysis was carried out in collaboration with Dr. Wooldridge.
Chapter 2

Related Studies on Stratospheric Particles and Heterogenous Chemistry

2.1 Characteristics of PSCs

As mentioned in Chapter 1, attention is currently focused upon polar stratospheric clouds because of their role in the ozone chemistry of the polar stratosphere.

The PSCs have been observed sporadically for more than a century [Stanford and Davis, 1974]. Although the clouds most frequently observed were of restricted size and limited duration in the Arctic, Stanford [1973] noted that an optically thin veil of clouds was observed persistently above Antarctica during the winters of 1950 and 1951.

A recently heightened interest in PSCs has arisen from satellite observations during the last decade, particularly those made by the SAM II instrument. McCormick et al. [1982] revealed the ubiquitous nature of the clouds in the Antarctic stratosphere observed by the SAM II instrument and demonstrated that they occurred when temperatures were close to the frost
point of ice.

Field measurements of Antarctic PSCs by Iwasaka [1985] indicated two distinct cloud particle classes. Studies by Toon et al. [1986], Crutzen and Arnold [1986] and McElroy et al. [1986b] suggested that PSCs might begin to form at temperatures above the ice frost point as frozen binary mixtures of HNO₃ and H₂O, probably in the form of HNO₃·3H₂O (NAT). Airborne measurements of Arctic PSCs [Poole and McCormick, 1988a; Poole et al., 1990] and SAM II Antarctic data [Poole and McCormick, 1988b] supported the two stage PSC formation process, delineated by the frost-point temperature.

Several lines of evidence [e.g., Toon et al., 1986; Poole and McCormick, 1988b] clearly indicated that the mean particle radius in type I PSCs would be near 1 µm: at temperatures from 2-6 K above the frost point, they found that particulate backscatter significantly exceeded that of the background aerosols, but that accompanying depolarization ratios were very small, a signature indicative of the particles having radii on the order of the laser wavelength (0.5 to 0.7 µm). At temperatures near the frost point, they found much larger backscatter enhancements as well as depolarization ratios which were typical of larger, cirrus-like ice crystals (Type II PSCs).

Data collected during recent Antarctic and Arctic field campaigns have provided additional insight into the PSC formation mechanism and physical characteristics. Analyses of AASE lidar data [Browell et al., 1990; Toon et al., 1990a] revealed two subclasses of Type I PSCs, both appearing at temperatures at/or below the equilibrium threshold for NAT. Type Ia PSCs are composed of nonspherical particles having a volume equivalent radius about 1.0 µm, while Type Ib clouds have spherical or nearly spherical particles with typical radii near 0.5 µm. Table 2.1 summarizes some characteristics of the PSC particles.
In situ measurements of total reactive nitrogen, total water, and aerosols during the AAOE [Fahey et al., 1989] indicated that concentrations of PSC particles with sizes between 0.8 and 2.5 μm are observed to be 10 to 100 times above background levels when temperatures are significantly above the ice frost. The dramatic NO$_x$\footnote{NO$_y$ includes the principal stratospheric nitrogen species as 

\[ \text{NO}_y = \text{NO} + \text{NO}_2 + \text{NO}_3 + 2(\text{N}_2\text{O}_5) + \text{HNO}_3 + \text{HO}_2\text{NO}_2 + \text{ClONO}_2 
+ \text{aerosol nitrate} + \ldots. \]}
enhancement inside PSCs confirms that the particles contain a substantial amount of nitrate, providing strong evidence that condensation of HNO$_3$ plays a critical role in PSC formation. Their NO$_y$ measurements also showed that these PSC particles form near NAT saturation (i.e., $S_{\text{NAT}} \geq 1.0$).

However, the AASE measurements indicated that the major increases in number and volume indicative of the main body of the NAT clouds are not seen in the Arctic investigations until 191 to 192 K, which corresponds to an apparent saturation ratio of HNO$_3$ with respect to NAT of 10 or greater ($S_{\text{NAT}} \geq 10$) [Kawa et al., 1992; Dye et al., 1992], contrary to the Antarctic findings [Fahey et al., 1989]. Their particle measurements using the Forward Scattering Spectrometer Probe (FSSP) are shown in Figure 2.1. Balloon-borne observations of Schlager et al. [1990] and Hofmann et al. [1990] in the Arctic bore results similar to those ER-2 measurements, also suggesting that extensive cloud particles formation is not observed until saturation ratio with respect NAT are near 10. Hence, there apparently exists a hemispherical difference on conditions of type I PSC formation. Also, as pointed out by Dye et al., an interesting footnote of the particles measurements is that the concentrations of NAT particles...
measured with the FSSP in well developed PSCs are larger than CN concentrations measured outside the PSCs [Wilson et al., 1992].

Another key feature of the polar ozone hole is the removal of HNO₃ (denitrification), observed in both the Arctic and Antarctica [Fahey et al., 1989; Dye et al., 1992; Kawa et al., 1992]. In particular, Dye et al. [1992] reported that a decrease in the number of particles was observed in regions in which the airmass was denitrified, i.e., the sum of all reactive nitrogen species, NOₓ, was reduced. Wofsy et al. [1990] suggested that ice particles in polar stratosphere descend into type I PSCs and accrete a coating of NAT that inhibits evaporation. The coated particles efficiently strip HNO₃ from the stratosphere, providing a mechanism of denitrification without dehydration. Alternatively, calculations by Toon et al. [1990b] did not assume scavenging of vapor by falling particles, yet suggested that HNO₃ and H₂O vapor removal can occur either separately or simultaneously, depending on the period and extent of cooling.

Preliminary measurements of the chemical composition of PSC particles were also carried out. Gandrud et al. [1989] conducted filter sampler measurements of cloud composition during the AAOE experiment. Using a dual filter system, they deduced the amount of nitrate in both the particulate and gas phases. Their data suggested that a substantial fraction of the available nitrate had been taken up on particles. Pueschel et al. [1989, 1992] collected aerosol particles using the wire and replicator impactors aboard the ER-2 aircraft and subsequently analyzed them for nitrate and chloride. Their results revealed a sharp dependence of condensed nitrate on temperature: nitrate-containing aerosols began to form at temperatures below about 193 K, in general agreement with expectations based on the thermodynamics of Type I NAT particles. They also concluded that the mass of HCl condensed in the particles was only 3% of the sulfuric
### Table 2.1. Polar Stratospheric Cloud Particles and Stratospheric Background Sulfate Aerosols

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Sulfate Aerosol</th>
<th>Type-I PSC</th>
<th>Type-II PSC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>La</td>
<td>lb</td>
</tr>
<tr>
<td>Physical State</td>
<td>Liquid or Slurry with Crystals</td>
<td>Solid NAT or NAD Nonspherical</td>
<td>Solid Crystal. Hexagonal or Cubic Basis</td>
</tr>
<tr>
<td>Particle Radius (µm)</td>
<td>0.05-0.1</td>
<td>~ 1</td>
<td>~ 0.5</td>
</tr>
<tr>
<td>Number (#/cm³)</td>
<td>1-10</td>
<td>0.1-10</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Surface Area (µm²/cm³)</td>
<td>0.5-2</td>
<td>0.5-5</td>
<td>0.1-8</td>
</tr>
<tr>
<td>Principal Composition</td>
<td>H₂SO₄/H₂O, ~75%/25%</td>
<td>HNO₃/H₂O, ~50%/50%</td>
<td>H₂O</td>
</tr>
<tr>
<td>Trace Composition</td>
<td>(NH₄)₂SO₄, NO₃⁻, HCl</td>
<td>HCl, H₂SO₄</td>
<td>HNO₃, HCl, H₂SO₄</td>
</tr>
</tbody>
</table>

41
Figure 2.1  Particle volume as a function of ambient temperature measured by FSSP during the AASe campaign. After Dye et al. [1992].
acid mass, suggesting that only a small fraction of the available chloride is incorporated into the particles. Additionally, based on the analysis of images from the replicator impactor as well as particle collection efficiency on the wire impactor, they deduced some information on the phase properties of the PSC particles. Using the same technique, Goodman et al. [1989] investigated microphysical characteristics of Antarctic stratospheric ice particles. Their results provided evidence that the ice crystals may be very effective in the removal of stratospheric chemicals.

Microphysical models for Type I PSCs have been developed by Poole and McCormick [1987], Hamill et al. [1988], and Wofsy et al. [1990]. Most of these models assumed that Type I PSCs nucleate on frozen background aerosol particles, probably consisting of sulfuric acid solid hydrates. The formation and growth of Type II have been discussed by Ramaswamy [1988] and Toon et al. [1989].

2.2 Characteristics of Stratospheric Sulfate Aerosols

The PSC formation occurs in the lower stratosphere at latitudes where the stratospheric aerosol layer [Junge, 1963] is found. The background stratospheric aerosols are believed to play a key role in the formation of PSCs [e.g., Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990; Molina et al., 1993], and they might also participate in heterogenous chemical reactions releasing active chlorine [Hofmann and Solomon, 1989; Molina et al., 1993].

Routine balloon-borne and lidar measurements of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ (sulfate) stratospheric aerosols have been conducted at several Northern Hemisphere sites since the early 1970s. These have been supplemented in a more global sense since the late 1970s with space-borne
observations by the SAM II, SAGE I, and SAGE II sensors.

The stratospheric sulfate aerosol layer consists of aqueous sulfuric acid with a mean diameter of about 0.1 μm and a concentration of from 1 to 10 cm\(^{-3}\) [Turco et al., 1982]. The size distribution of the background stratospheric aerosols is given by extensive global measurements in a log-normal function of the form [Rosen et al., 1975],

\[
\frac{dN(r)}{dr} = \frac{N_0}{r(2\pi)^{1/2}\ln \sigma} \exp \left[ - \frac{\ln^2(r/r_g)}{2\ln^2 \sigma} \right]
\]  

(2.1)

with \(r_g = 0.0725\) μm, \(\sigma = 1.86\), and \(N_0 = 10\) particles cm\(^{-3}\). The total surface area for the normal background aerosols is between 0.5 and 2.0 μm\(^2\) cm\(^{-3}\), depending on altitude and latitude. Table 2.1 also summarizes some characteristics of the background stratospheric sulfate aerosols.

Calculations by Hamill [1975] showed that stratospheric aerosol droplets grow by binary condensation of H\(_2\)O and H\(_2\)SO\(_4\) vapors and that change in temperature will affect the composition of the droplets. Steele and Hamill [1981] and Steele et al. [1983] indicated that at mid-latitudes the sulfate aerosols are composed of 60-80 % wt aqueous sulfuric acid, while a much more dilute solution (10% to 30%) is expected at high-latitudes. Measurements of compositions of sulfate aerosols has also been made using the evaporation technique to measure the boiling point as a function of atmospheric pressure [Rosen, 1971; Hofmann and Solomon, 1989].

It should be noted that there is no direct observational evidence on freezing of the sulfate aerosols in the stratosphere. The analysis of the FSSP particle measurements [Dye et al., 1992] suggested that in the Arctic a major fraction of the sulfate aerosols remain liquid down to temperatures at least as low as 193 K. Balloon-borne measurements [Schlager et al., 1990;
Hofmann et al., 1990] also indicated that relatively few sulfate aerosols are frozen at HNO$_3$ saturation and that further cooling (to about 192 K) is required for the aerosols to freeze and serve as PSC nuclei. In recent AASE II observations [Toon et al., 1993], freezing of the sulfate aerosols at temperatures near the ice frost point was further documented.

Major volcanic eruptions may significantly increase sulfuric loading in the stratosphere. The impact of major volcanic eruptions is very large initially and may persist for several years. The El Chichon eruption of 1982 increased the stratospheric aerosol mixing ratios nearly 2 orders of magnitude above the background level. Hofmann [1987] reported that a few months after the El Chichon eruption a maximum surface area density of about 50 $\mu$m$^2$ cm$^{-3}$ was observed in the dense aerosol layer between 20 and 25 km in the north America. The El Chichon eruption also displayed large optical effects and perturbations on remote sensing instruments [McCormick et al., 1984]. Mt. Pinatubo in the Philippines erupted violently in June 1991, injecting a cloud of sulfur dioxide into the stratosphere. Analysis of early satellite observations suggest that Mt. Pinatubo injected two to three times as much as sulfur into the stratosphere as El Chichon [Bluth et al., 1992; McCormick and Veiga, 1992]. A relative short-term increase in total sulfate surface area of a factor of 10 and 100 after the Mt. Pinatubo eruption was observed [Deshler et al., 1992; Sheridan et al., 1992].

Model calculations [Hofmann and Solomon, 1989; Brasseur et al., 1990] have demonstrated that the heterogeneous reaction between $\text{N}_2\text{O}_5$ and $\text{H}_2\text{O}$ occurring on the surfaces of the El Chichon aerosols may account for the larger-than-expected ozone trend. Direct evidence for this heterogeneous conversion, i.e., the shifts in the trace gas concentrations in the El Chichon cloud, has also been collected [Arnold et al., 1991]. In addition, recent AASE II data
even suggested that at cold enough temperatures heterogeneous reactions on Mt. Pinatubo aerosols could be as efficient as those on PSCs. Toon et al. [1993] have presented measurements of HCl and ClONO$_2$ integrated column abundances. Reductions in both species were observed, in spite of the fact that no indication of PSC formation was observed. Such results raise an interesting point about potential chlorine activation during the early polar winter.

2.3 Laboratory Measurements

Recent laboratory studies have greatly improved our understanding on PSC and heterogeneous chemistry.

Vapor pressures of the HNO$_3$/H$_2$O binary system were originally investigated by Hanson and Mauersberger [1988a]. Their laboratory results corroborated that PSCs consisting of NAT crystals may form at temperatures several degrees above the ice frost point. Worsnop et al. [1993] further explored the HNO$_3$/H$_2$O system, showing that, in addition to NAT, HNO$_3$$\cdot$2H$_2$O (nitric acid dihydrate, NAD) crystals may form under stratospheric conditions if nucleated and if the more thermodynamically stable NAT is not present. Infrared absorption spectra of amorphous and crystalline films of H$_2$O/HNO$_3$ mixtures [Ritzhaupt and Devlin, 1991; Tolbert and Middlebrook, 1990; Middlebrook et al., 1992; Smith et al., 1991; Koehler et al., 1992] as well as of small NAT and NAD aerosol particles [Barton et al., 1993] have been reported.

The interaction of HCl with proposed PSC materials has been a subject of considerable investigations [Hanson and Mauersberger, 1988b; Wofsy et al., 1988; Wolff et al., 1989; Elliott et al., 1990; Marti et al., 1991; Hanson and Ravishankara, 1992; Abbatt and Molina, 1992;
Abbatt et al., 1992; Chu and Leu, 1993], with emphasis from bulk HCl solubility to surface concentration. Recent studies [Hanson and Ravishankara, 1991; Abbatt and Molina, 1992; Chu et al., 1993] have shown that at low HCl partial pressures, representative of those found in the stratosphere, the HCl uptake corresponds to submonolayer coverage on PSC particles and that for high HCl partial pressures large uptake occurs as a result of surface melting. The formation of HCl hydrates under current stratospheric conditions was concluded to be improbable, based on vapor pressure data of the HCl/H$_2$O system [Hanson and Mauersberger, 1990].

Since Molina et al. [1987] first reported the heterogeneous reactions on ice, there have been many measurements of the heterogeneous reaction probabilities of ClONO$_2$ and N$_2$O$_5$ with H$_2$O and HCl on ice and NAT; these results are summarized in Tables 2.2 and 2.3. In particular, those heterogeneous reactions have been shown to occur readily at stratospheric concentrations of ClONO$_2$ and HCl [Hanson and Ravishankara, 1991, 1992], and to vary strongly as a function of the thermodynamic state of the NAT surfaces [Abbatt and Molina, 1992].

Laboratory experiments were also performed to investigate HCl and HNO$_3$ solubilities in background sulfate aerosols. Reihs et al. [1990] reported vapor pressures of nitric acid in sulfuric acid solutions ranging from 58 to 87 weight percent over a temperature range from 188 to 240 K. Van Doren et al. [1991] examined uptake of nitric acid by aqueous sulfuric acid droplets at 283 K. The uptake of HCl in aqueous sulfuric acid droplets was studied by Watson et al. [1990] at 283 K. Also, the results obtained by Tolbert [1992] for a 60 % H$_2$SO$_4$ solution at 203 K indicate that stratospheric aerosol containing 60-75 % sulfuric acid has a very low equilibrium HCl concentration (less than $10^{-7}$ M).

Reaction between N$_2$O$_5$ and H$_2$O has been shown to occur efficiently on sulfuric acid
Table 2.2. Reaction Probabilities for the Hydrolysis of ClONO$_2$ and N$_2$O$_5$ on PSC Surfaces

<table>
<thead>
<tr>
<th></th>
<th>Ice</th>
<th>NAT</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClONO$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molina et al., 1987</td>
<td>(0.02)</td>
<td></td>
</tr>
<tr>
<td>Tolbert et al., 1987</td>
<td>(0.009)</td>
<td></td>
</tr>
<tr>
<td>Leu, 1988a</td>
<td>(0.06)</td>
<td></td>
</tr>
<tr>
<td>Moore et al., 1990</td>
<td></td>
<td>0.02*</td>
</tr>
<tr>
<td>Leu et al., 1991</td>
<td></td>
<td>0.001*</td>
</tr>
<tr>
<td>Hanson and Ravishankara, 1992</td>
<td>0.3</td>
<td>0.006</td>
</tr>
<tr>
<td>Abbatt and Molina, 1992a</td>
<td>&gt;0.02</td>
<td>0.001-0.002*</td>
</tr>
<tr>
<td>N$_2$O$_5$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tolbert et al., 1988b</td>
<td>(&gt;0.001)</td>
<td></td>
</tr>
<tr>
<td>Leu, 1988b</td>
<td>(0.028)</td>
<td></td>
</tr>
<tr>
<td>Quinlan et al., 1990</td>
<td>(0.03)</td>
<td>(0/015)</td>
</tr>
<tr>
<td>Hanson and Ravishankara, 1991b</td>
<td>0.024</td>
<td>0.0006</td>
</tr>
<tr>
<td>Kenner et al., 1992b</td>
<td>0.01-0.02</td>
<td></td>
</tr>
</tbody>
</table>

*Value on "water-rich" NAT. Values on "pure" NAT are considerably lower.

solutions, with a reaction probability (~0.1) that is relatively independent of temperature and of H$_2$SO$_4$ concentration [Mozurkewich and Calvert, 1988; Hanson and Ravishankara, 1991; Van Doren et al., 1991]. Thus, this reaction may represent an important loss process for NO$_x$ on a global scale. The reactions of ClONO$_2$ with H$_2$O and HCl on sulfuric acid solutions, on the other hand, have been shown to vary strongly with sulfuric acid concentrations [Tolbert et al., 1988; Hanson and Ravishankara, 1991], and are unlikely a source of global perturbed stratospheric chemistry. At very cold temperatures slightly preceding PSC formation, the background sulfate aerosols may take up enough HCl such that the reaction between ClONO$_2$ and HCl plays a role in chlorine activation [Molina et al., 1993]. This seems to be supported by the recent AASE II observations [Toon et al., 1993].
### Table 2.3. Reaction Probabilities Involving HCl on PSC Surfaces

<table>
<thead>
<tr>
<th></th>
<th>Ice</th>
<th>NAT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>ClONO$_2$ + HCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molina et al., 1987</td>
<td>0.05-0.1</td>
<td></td>
</tr>
<tr>
<td>Leu, 1988a</td>
<td>0.06-0.3</td>
<td></td>
</tr>
<tr>
<td>Moore et al., 1990</td>
<td></td>
<td>0.06-1.0</td>
</tr>
<tr>
<td>Leu et al., 1991</td>
<td></td>
<td>0.1</td>
</tr>
<tr>
<td>Hanson and Ravishankara, 1991b</td>
<td>a</td>
<td>0.3</td>
</tr>
<tr>
<td>Abbatt and Molina, 1992b</td>
<td>&gt;0.2</td>
<td>&gt;0.2$^b$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>N$_2$O$_5$ + HCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tolbert et al., 1988b</td>
<td>&gt;0.003</td>
<td></td>
</tr>
<tr>
<td>Leu, 1988b</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Hanson and Ravishankara, 1991b</td>
<td>a</td>
<td>0.0032</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>HOCl + HCl</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hanson and Ravishankara, 1992</td>
<td>&gt;0.3</td>
<td>0.1</td>
</tr>
<tr>
<td>Abbatt and Molina, 1992a</td>
<td>0.16-0.24</td>
<td>0.17$^b$</td>
</tr>
</tbody>
</table>

$^a$No enhancement in $\gamma$ was observed over reaction on pure ice without HCl.

$^b$Value on "water-rich"-NAT. Value is two orders of magnitude lower for "HNO$_3$-rich"-NAT.
Chapter 3

Physical Chemistry of Two-Component Acid Systems and Stratospheric Implications

In this chapter, thermodynamic properties (such as melting points, enthalpies of fusion, etc.) for acids relevant to the stratosphere (HCl, HNO₃, and H₂SO₄) are studied using laboratory-assembled apparatus for electrical conductivity and differential thermal analysis (DTA), and using a commercial differential scanning calorimeter (DSC). Vapor pressures and infrared spectra of liquid and supercooled solutions, and of liquid-solid and solid-solid coexistence mixtures for the HCl/H₂O and H₂SO₄/H₂O binary systems are investigated. Equilibrium constants and standard enthalpies of formation for the pure crystalline hydrates of those acids as well as their corresponding liquid compositions are determined from our laboratory measurements and standard literature data. A theoretical approach, which allows determination of thermodynamic equilibrium for two adjacent hydrates and for the coexistence system involving a hydrate and ice, is presented in terms of chemical equilibrium principles and compared with the experimental data
for thermodynamic consistence.

3.1 Background

The two fundamental thermodynamic principles that guide the study of binary mixtures are the phase rule and the Gibbs-Duhem relation. In this section, a general description of these two principles pertaining to binary systems is reviewed.

3.1.1 The Phase Rule

The Gibbs phase rule for bulk phases in equilibrium states that the variance or degrees of freedom of a system \( F \), the number of components \( C \), and the number of phases \( P \) are related by

\[
F = C - P + 2 \tag{3.1}
\]

The degrees of freedom of a system in equilibrium are the number of intensive variables which can be independently varied without causing the system to depart from equilibrium.

In a binary system \( C = 2 \) the intensive variables are temperature, pressure and composition of each phase. For a single hydrate and vapor, \( P = 2 \), so \( F = 2 \), i.e., there are two degrees of freedom. This can be best demonstrated in Figure 3.1, the phase diagram of the HNO\(_3\)/H\(_2\)O system, showing that nitric acid trihydrate (NAT) can exist over a range of H\(_2\)O and HNO\(_3\) vapor pressures and temperatures. When two hydrates are in equilibrium with the vapor, there are three phases, so \( F = 1 \): there is a single degree of freedom. Therefore, for a given
Figure 3.1 HNO$_3$ vs. H$_2$O vapor pressures for the HNO$_3$/H$_2$O binary system. The dashed lines are isotherms, and the solid lines represent coexistence conditions for two condensed phases. After Worsnop et al. [1993].
temperature, the vapor pressure must be uniquely determined. In the phase diagram the lines representing the coexistence of two adjacent hydrates delineate regions of stability of various phases. For the HNO$_3$/H$_2$O binary system, the coexistence lines of mono-/trihydrate and ice/trihydrate define the stability region of NAT. Hence, at a given temperature NAT can have a range of compositions differing slightly from the stoichiometric $3:1$ mole fraction ratio; each composition leads to a specific set of vapor pressures for H$_2$O and HNO$_3$. Also as shown in Figure 3.1, Q represents the quadruple point for vapor, monohydrate, dihydrate, and trihydrate, as suggested by Worsnop et al. [1993]; there are no degrees of freedom at this point.

### 3.1.2 The Gibbs-Duhem Relation

For a binary system at a constant temperature the Gibbs-Duhem equation relates the variation of the vapor pressure of one of the components, $P_1$, to the variation of the vapor pressure of the other component, $P_2$:

$$
\frac{d(\ln p_1)}{d(\ln p_2)} = -\frac{x_2}{x_1} = -\frac{(1-x_1)}{x_1} \quad (3.2)
$$

where $x_1$ and $x_2$ are the mole fractions for the two components.

For liquid solutions, such a relation permits calculation of vapor pressures of one component, knowing the variation of vapor pressures of the other component with composition. This method has been employed previously to determine the vapor pressures of the supercooled HNO$_3$/H$_2$O system [Clavelin and Mirabel, 1979; Hanson, 1990] and will be used below to determine H$_2$SO$_4$ vapor pressures for supercooled H$_2$SO$_4$/H$_2$O solutions.

For a single condensed phase in a binary system, the Gibbs-Duhem relation can be
expressed at a constant temperature as

\[
\frac{d(\ln P_{\text{acid}})}{d(\ln P_{\text{w}})} = -n
\]  (3.3)

where \( n \) is the acid/water ratio in the hydrate. For the \( \text{HNO}_3/\text{H}_2\text{O} \) binary system, the stoichiometric ratios of 3, 2, and 1 correspond to the phases of nitric acid trihydrate (NAT), dihydrate, and monohydrate, respectively. It also follows from this equation that isotherms in Figure 3.1 should be almost straight lines with slopes very close to \(-3\), \(-2\), and \(-1\) in the stability regions of NAT, NAD, and NAM. As a matter of fact, as originally reported by Hanson and Mauersburger [1988] for NAT, small departures from the stoichiometric 3:1 mole fraction ratio were not observable in the slope measurements due to experimental uncertainties (see also section 4.4.1), and, therefore, composition changes of NAT with its stability regime ought to be very small. A small change in the \( \text{HNO}_3/\text{H}_2\text{O} \) ratio (or composition change), on the other hand, can result in a significant change in the chemical potentials and hence the vapor pressures of this system. Generally, depending on the \( \text{H}_2\text{O} \) vapor pressure, NAT can be in equilibrium with ice at one extreme, and with the monohydrate at the other. The former is often refereed as "\( \text{H}_2\text{O-} \) rich" NAT, whereas the latter is refereed as "\( \text{HNO}_3\)-rich" NAT [Molina, 1993].

3.2 Experimental

3.2.1 Vapor Pressure Measurements

Vapor pressures of the binary systems (\( \text{H}_2\text{SO}_4/\text{H}_2\text{O}, \) \( \text{HCl}/\text{H}_2\text{O}, \) and \( \text{HNO}_3/\text{H}_2\text{O} \)) were measured using a static technique, similar to that employed by Hanson and Mauersberger [1988c] for studying the \( \text{HNO}_3/\text{H}_2\text{O} \) system.
Figure 3.2 Schematic diagram of the experimental apparatus employed in the vapor pressure measurements.
The apparatus, shown in Figure 3.2, consisted of a removable glass sample vessel, pumping-out lines, a temperature controller device, and a mass spectrometer (Ametek MA200). The acid mixture was placed at the bottom of the sample vessel where the cold region was 3 to 4 cm high and 6 cm in diameter. Inside the sample vessel, a magnetic bar enclosed in glass was used to stir the acid mixture in order to ensure a homogeneous composition for the liquid. The sample vessel was immersed in a temperature controlled ethanol bath regulated by a combination of liquid nitrogen cooling and resistive heating to about ±0.1°C. The temperature was monitored by a thermocouple attached to the exterior of the vessel. The thermocouple was calibrated both at the ice point and at the temperature of dry ice/acetone mixture and had an accuracy of ±0.2°C. Both mass spectrometer data and temperature data were acquired using a microcomputer.

Vapor samples were drawn through a 0.4 cm i.d. probe tube (ending ~ 2.5 cm above the sample surface) kept at room temperature by circulating water through a jacket surrounding the tube. A glass vacuum line free of teflon and metal components fed the gas samples to the mass spectrometer through an orifice of about 2 mm in diameter. Inside the mass spectrometer chamber, a polished stainless steel vessel filled with liquid nitrogen was employed to reduced background signals. The effect of thermal transpiration along the transition to the room temperature vacuum line was taken into account using the method suggested by Hanson and Mauersberger [1988].

The H₂O pressure was calibrated using the literature values of pure ice [Jansco et al., 1970]. The mass spectrometer was calibrated for HNO₃ using the vapor pressures of supercooled HNO₃/H₂O solutions from Hanson and Mauersberger [1988] and for HCl using the extrapolated
data of HCl/H$_2$O solutions from Fritz and Fuget [1956]. These extrapolated HCl vapor pressures are in reasonable agreement with the measurements of Hanson and Mauersberger [1990] for the supercooled HCl/H$_2$O solutions. HNO$_3$, HCl, and H$_2$O were monitored at mass peaks of 46, 36, and 18, respectively. For all measurements the mass spectrometer signals were continuously monitored. For measurements involving liquid and supercooled solutions it normally took less than a few minutes to reach steady state, whereas for measurements involving solid substrates it took up to several hours to reach equilibrium. Small background signals were subtracted from the steady state readings. The experimental detection limits were about $10^{-7}$ Torr for HNO$_3$ and HCl and about $10^{-5}$ Torr for H$_2$O.

### 3.2.2 Calorimetric and Conductivity Measurements

**Differential Scanning Calorimetry (DSC)**

Differential Scanning Calorimetry (DSC) was employed to measure transitions between thermodynamically distinct bulk phases. To prevent possible condensation of H$_2$O onto the sample at low temperatures or evaporation of the substrate as well as to prevent corrosion, titanium or gold plated capsules, which may be almost completely sealed, were used to hold the solutions.

Details of the theory and design of differential scanning calorimeters have been given by Watson et al. [1964] and by O’Neill [1964]. In the present study a commercial calorimeter (Perkin-Elmer DSC-7) was used. As shown schematically in Figure 3.3 (a), the operation of the DSC is based exclusively on the so called energy compensated "null-balance principle" in which energy absorbed or evolved by the sample is compensated by adding or subtracting an equivalent
Figure 3.3 Schematic representation of the two principal thermal analysis systems.
amount of electrical energy to a heater located in the sample holder. The energy which is necessary to keep the sample holder temperature identical to that of the reference holder thus also provides calorimetric information such as enthalpies of fusion.

Calibration of the DSC can be made using different standards, and the most frequently used calibrant is cyclohexane, which has two transition points, at -87.06 and at 6.54°C. The DSC cooling or warming rates were generally 4°C/min, except noticed otherwise. Temperature uncertainty in the DSC experiments was less than ±0.5°C, and uncertainty in enthalpies of fusion was less 10%.

Figure 3.4 shows an example of DSC cooling and warming runs for pure water. The measured transition energy in this case is 332.95 J/g for the melting of ice, which is only 1% less than the literature value (333.88 J/g) [Rogers, 1979].

Differential Thermal Analysis (DTA)

We initially built a DTA apparatus to investigate freezing points and phase diagrams for the binary acid systems. Shown schematically in Figure 3.3 (b) is a laboratory-assembled design in which a sample and an inert reference (normally being left empty) were placed in small glass tubes inserted into a temperature-controlled aluminum block. The thermocouple wires were enclosed in a glass capillary tubes of about 0.1 mm in diameter.

An important different between DSC and DTA systems is that in the latter the sample and reference are provided with a single heat source, hence the DTA technique yields inherently less quantitative information than that of DSC. Our DTA components are generally larger than those
Figure 3.4 An example of DSC run for cooling a pure water and subsequent warming. The cooling rate is 4°C/min, and the warming rate is 10°C/min (the larger heating rate is necessary to increase sensitivity; it causes the ice-melting peaks to appear at a higher temperature).
Figure 3.5 DTA warming curves for two HCl solutions of 10 and 15 wt %. The peaks near -74°C correspond to the ice/hexahydrate eutectic, whereas the peaks at warmer temperatures represent melting of ice.
Figure 3.6 Schematic diagram of the experimental apparatus employed in the electrical conductivity measurements.
Figure 3.7 Conductance variation with temperature when cooling a 0.1 wt % HCl solution and warming.
in commercial devices and hence are less sensitive. Figure 3.5 shows examples of DTA warming curves for two HCl/H₂O solutions.

*Electrical Conductivity*

This is a sensitive method to determine if even a small amount of an electrolytic solution remains liquid. As shown schematically in Figure 3.6, the apparatus consisted of a commercial low-frequency conductivity meter (YSI Model 35), which employs pulses of alternating polarity at 1000 Hz to cancel charge storage effects, and a simple probe consisting of parallel 0.5-mm-diameter platinum wires held ~ 3 mm apart by a glass envelope, with the lower ~ 2 mm of the wires being exposed. The analog outputs of the meter and of a thermocouple thermometer, with its glass-encased probe immersed in the sample, were digitized and recorded by a microcomputer. Figure 3.7 shows an example of the conductance variation with temperature when cooling a 0.8 wt % HCl solution and subsequent warming.

### 3.2.3 Infrared Spectroscopic Measurements

Figure 3.8 shows schematically the apparatus used for infrared spectroscopic studies. The samples were prepared by placing a drop of bulk solution between infrared transmitting windows (discs of AgCl or ZnSe) and, then, pressing the windows to spread the drop into a film of a few μm thickness. The backing plate for the windows was a temperature-controlled copper bar and the assembly was purged to prevent condensation. The temperature calibration of the system was
Figure 3.8  Schematic diagram of the cell used for infrared transmission measurements.
verified by observing the phase transition of a cyclohexane film at 186 K. Data was acquired using a Nicolet 800 Fourier transform spectrometer at 2 cm\(^{-1}\) resolution.

### 3.2.4 Sample Preparation and Supercooling Information

For the binary systems (H\(_2\)SO\(_4\)/H\(_2\)O, HCl/H\(_2\)O, and HNO\(_3\)/H\(_2\)O) bulk liquid mixtures were prepared by diluting 95.6 wt % sulfuric acid solutions with distilled water. The liquid compositions were analyzed either by standard acid-based titration or by density measurements at room temperature. The accuracy of both methods was about ±0.1% by weight. Typically, 3 cm\(^3\) of liquid was used for the vapor pressure measurements, while less than 0.03 cm\(^3\) was employed for infrared spectroscopy, thermal analysis, and electrical conductivity. For most experiments in this study, the liquid compositions were analyzed before and after each experiment.

Although it is not the main focus of this thesis, some useful information on freezing and supercooling of the binary systems is derived from the calorimetric, conductance, and vapor pressure measurements. In the mass spectrometer, momentary surges in both H\(_2\)O and N\(_2\) signals were observed associated with solid formation, which may be due to the exothermicity or outgassing of the process. Because the sample volume employed in vapor pressure measurements was much larger than those employed in the calorimetric and conductance measurements and because the cooling rate in the vapor pressure measurements was much slow, some preliminary information on the effect of sample size and cooling rate on freezing and supercooling was deduced.
3.3 The $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ Binary System

3.3.1 Introduction

As mentioned in section 2.2, the stratospheric background aerosol layer, which exists at altitudes between about 10 and 25 km, consists mainly of particles of aqueous sulfuric acid with a mean diameter of $\sim 0.1 \mu m$ and a concentration from 1 to 10 cm$^{-3}$ [Turco, 1982]. Major volcanic eruptions, such as the 1991 eruption of Mt. Pinatubo, may increase the background concentration by more than an order of magnitude. Recent interest in stratospheric aerosols has focused on their role in the occurrence of the Antarctic ozone 'hole' as well as in global ozone loss, through heterogeneous chemical processes. These background sulfate aerosols are important in heterogeneous chemistry for at least two reasons: (1) they may act as nuclei for the formation of polar stratospheric clouds (PSCs) [Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990; Molina et al., 1993]; and (2) they may participate directly in heterogeneous reactions involving ClONO$_2$, HCl, N$_2$O$_5$, and H$_2$O to promote the release of active chlorine and to affect the stratospheric NO$_x$ budget [Molina et al., 1987; Rodriguez et al., 1988; Tolbert et al., 1988; Hofmann and Solomon, 1989; Wolff and Mulvaney, 1991; Hanson and Ravishankara, 1991].

A number of authors [Pickering, 1890; Hulzmann and Biltz, 1934; Gable et al., 1950; Hornung et al., 1956; Vuillard, 1957; Giauque et al., 1960; Mootz and Merschenz-Quack, 1987] have investigated the melting points and phase equilibria of the sulfuric acid/water binary system, establishing the existence of several crystalline hydrates, namely mono-, di-, tri-, tetra-, hemihexa-, and octahydrate. Giauque et al. [1960] reported chemical potentials and various other
thermodynamic properties of aqueous sulfuric acid solutions and crystalline hydrates, and their results were used by Gmitro and Vermeulen [1964] and by Jaecker-Voirol et al. [1990a,b] to calculate vapor pressures of water and sulfuric acid. Recently, a more comprehensive summary of thermodynamic properties of the aqueous sulfuric acid system has been reported by Zeleznik [1991]. In addition, a number of spectroscopic studies have been carried out for this binary system [Giguère and Savoie, 1960; Querry et al., 1974; Palmer and Williams, 1975].

At present, however, assessments of the role of sulfuric acid aerosols in the formation of PSCs and in promoting heterogeneous chemistry are still limited by the lack of reliable knowledge of thermodynamic properties of the H₂SO₄/H₂O binary system under conditions characteristic of the stratosphere. For example, no direct measurements had been made of vapor pressures for liquid and supercooled solutions at stratospheric temperatures; such measurements are needed in order to verify the earlier theoretical predictions.

In this section laboratory experiments are presented in order to investigate the physical chemistry of the H₂SO₄/H₂O binary system under conditions characteristic of the stratosphere. Water vapor pressures of sulfuric acid solutions (20 to 70 wt %), and of liquid-solid and solid-solid phase coexistence systems have been measured by mass spectrometry at temperatures between 190 and 240 K. Infrared spectra of the liquid, supercooled liquid, and crystalline hydrates of this system have also been investigated.

3.3.2 Vapor Pressures

Liquid and Supercooled liquid

H₂O vapor pressures, Pᵥ, of liquid and supercooled sulfuric acid solutions were measured
TABLE 3.1. Coefficients from a Least-Squares Fit of log $P_w = A - B/T$ for Water Vapor Pressures in the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ Binary System

<table>
<thead>
<tr>
<th>wt % $\text{H}_2\text{SO}_4$</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>33.85</td>
<td>9.735</td>
<td>2514</td>
</tr>
<tr>
<td>35.7</td>
<td>9.674</td>
<td>2496</td>
</tr>
<tr>
<td>37.5</td>
<td>9.523</td>
<td>2485</td>
</tr>
<tr>
<td>44.2</td>
<td>9.268</td>
<td>2488</td>
</tr>
<tr>
<td>56.6</td>
<td>9.466</td>
<td>2623</td>
</tr>
<tr>
<td>62.6</td>
<td>9.543</td>
<td>2710</td>
</tr>
<tr>
<td>67.8</td>
<td>9.479</td>
<td>2785</td>
</tr>
<tr>
<td>70.0</td>
<td>9.710</td>
<td>2831</td>
</tr>
<tr>
<td>tetra-/dihydrate coexistence</td>
<td>11.502</td>
<td>3236</td>
</tr>
</tbody>
</table>

* $P_w$: Torr

$T$: Kelvin
Figure 3.9  Water vapor pressures of liquid and supercooled liquid. Weight percentages of H$_2$SO$_4$ are labeled in the figure. The solid lines are the least squares fits of the experimental data (open circles) from this work. The dashed-dotted lines are data taken from Jaecker-Voirol et al. [1990a, b], and the dashed lines from Gmitro and Vermeulen [1964].
for H$_2$SO$_4$ contents ranging from 20 to 70 wt %. Coefficients of the least squares fits in the form of log $P_w = A - B/T$ for the cases investigated here are summarized in Table 3.1. Figure 3.9 shows the Clausius-Clapeyron plot for some selected H$_2$SO$_4$ concentrations: the open circles label experimental data points and the solid lines are the least squares fits to the data. As shown in the figure, over the relatively narrow temperature range investigated the temperature dependence of the H$_2$O vapor pressures for a given composition is well described by the linear equation.

The dashed-dotted lines in Figure 3.9 represent the estimates based on the work of Jaecker-Voirol et al. [1990a, b] and the dashed lines based on that of Gmitro and Vermeulen [1964]. Both sets of data were derived from thermodynamic measurements other than vapor pressures, and are in poor agreement with our measurements for the more concentrated solutions (~ 60 wt %); in the first set, the Clausius-Clapeyron equation was integrated assuming a constant heat capacity difference, whereas in the second set the heat capacity difference was linearized with temperature. In fact, the heat capacity of sulfuric acid solutions changes with temperature and composition in a complicated manner [Hornung et al., 1956; Giauque et al., 1960; Gmitro and Vermeulen, 1964; Mootz and Merschenz-Quack, 1987; Jaecker-Voirol et al., 1990a, b; Zeleznik, 1991], because of the occurrence of several ionization reactions, as discussed below in the "Infrared Spectra" section. For the more dilute solutions (≤ 37 wt %) the results based on the report of Gmitro and Vermeulen [1964] are in reasonable agreement with our data, whereas those based on Jaecker-Voirol et al. [1990a, b] yield significantly lower water vapor pressures. These lower values are clearly in error, because for such dilute solutions the H$_2$O vapor pressure can be predicted accurately at one particular temperature, namely at the equilibrium freezing point: the H$_2$O vapor pressure is practically the same as that of pure ice at that temperature. For
Figure 3.10 Water vapor pressures as a function of $\text{H}_2\text{SO}_4$ wt % at 200 and 250 K. The solid lines are results from this study, while the dashed lines are calculated using the tabulated relative chemical potentials reported by Zeleznik [1991].
those compositions the solid phase that is in equilibrium with the liquid at the freezing point is ice; consequently, the chemical potential of H$_2$O -and hence the H$_2$O vapor pressure- has the same value in those two phases. That is, since the ice phase in consideration has only trace amounts of H$_2$SO$_4$, its H$_2$O chemical potential is essentially equal to that of pure ice. Within experimental error (i.e., within about 5 %) this prediction was borne out by our measurements (see also Figure 3.11).

When extrapolated to room temperature, our vapor pressures agree well with literature values [Hornung and Giauque, 1955]. Vapor pressures over 68.4 to 85 wt % H$_2$SO$_4$ were also measured by Daudt [1923] down to 220 K: his 68.4 wt % values fall essentially on the same line as our measurements. Also, as shown in Figure 3.10, our results are in good agreement with the H$_2$O vapor pressures calculated using the relative chemical potentials tabulated by Zeleznik [1991] at 200 and 250 K (within 20%).

For convenience in presentation, our experimental water vapor pressures were fitted as a function of the H$_2$SO$_4$ concentration as follows:

$$\log P_w = a_1 + a_2w + a_3w^2 + a_4w^3$$  \hspace{1cm} (3.4)

where $w$ is the H$_2$SO$_4$ weight fraction (i.e., $w = 0.4$ for a 40 wt % solution). The coefficients $a_i$ ($i = 1, 4$) are given in the form of $a_i = A + B/T$ in Table 3.2. In general, there is less than 10 % difference between the values calculated using equation (1) and the experimental data. This expression is valid only for the acid concentration range employed in our measurements, i.e., from 20 to 70 wt % H$_2$SO$_4$.

As mentioned before, vapor pressures of sulfuric acid can be calculated from the measured water vapor pressures by the use of Gibbs-Duhem equation. The water vapor pressures
TABLE 3.2. Values of the Coefficients for Equation (3.4)*

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B x 10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₁</td>
<td>9.60</td>
<td>-2.44</td>
</tr>
<tr>
<td>a₂</td>
<td>4.04</td>
<td>-0.77</td>
</tr>
<tr>
<td>a₃</td>
<td>-16.82</td>
<td>3.19</td>
</tr>
<tr>
<td>a₄</td>
<td>16.03</td>
<td>-4.20</td>
</tr>
</tbody>
</table>

* \( \log P_w = a_1 + a_2w + a_3w^2 + a_4w^3 \)

\( a_i = A + B/T \) \((i = 1, 4)\)

\( P_w: \) Torr

\( T: \) Kelvin
TABLE 3.3. Values of the Coefficients to Be Used in Equation (3.5)

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$a_3$</th>
<th>$a_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>273</td>
<td>4.896</td>
<td>-38.492</td>
<td>64.155</td>
<td>-29.943</td>
</tr>
<tr>
<td>253</td>
<td>0.849</td>
<td>-23.849</td>
<td>42.741</td>
<td>-19.660</td>
</tr>
<tr>
<td>233</td>
<td>-3.821</td>
<td>-6.940</td>
<td>17.931</td>
<td>-7.717</td>
</tr>
</tbody>
</table>
Figure 3.11  Sulfuric acid vapor pressures calculated from the Gibbs-Duhem equation (solid lines). The data from Jaecker-Voirol et al. [1990a, b] are plotted as long dashed lines for comparison.
derived from the present experiments can also be fitted as a function of the H₂O mole fraction,

\[
\log P_w = a_1 + a_2x_w^2 + a_2x_w^2 + a_3x_w^3
\]  

(3.5)

where the coefficients \(a_i\) (i = 1, 4) are given in Table 3.3 for two temperatures. Errors arising from the curve fitting were in general less than 10%. Subsequently, equation (3.2) can be integrated at constant temperature to obtain the sulfuric acid vapor pressures,

\[
P_s = P_{o,s}\exp[A_1x_w + A_2x_w^2/2 + A_3x_4^3/3 - A_4\log(1 - x_w)]
\]  

(3.6)

where \(x_w\) is the mole fraction of H₂O and \(A_i\) (i = 1, 4) are the integration constants. The pure sulfuric acid vapor pressure, \(P_{o,s}\), is given by Ayers et al. [1980]. Results of the calculated sulfuric acid vapor pressures are depicted in Figure 3.11. Also shown in this figure are the data taken from Jaecker-Voirol et al. [1990]. Although similar lines were also obtained by Gmitro and Vermeulen [1964], they are not plotted here for the sake of clarity. It should be pointed out that there is a significant uncertainty in calculating the H₂SO₄ vapor pressures using the present H₂O partial pressures and equation (3.2): this equation includes integrating H₂O vapor pressure with respect to H₂SO₄ mole fraction up to unity (i.e., 100 wt % H₂SO₄) and, as a result, the present H₂O vapor pressures need to be extrapolated beyond the measured highest concentration of 70 wt %.

*Freezing Envelopes*

According to the phase rule described earlier, the thermodynamic state for a three-phase equilibrium in a binary system is uniquely determined at a given temperature (i.e., \(C = 2\) and \(P = 3\) so that \(F = 1\), according to equation (3.1)). The three phases can be a vapor and two
Figure 3.12 Water vapor pressures over partially frozen mixtures. The open circles and solid line are results from this study, while the dotted line is the intersections of the Jaecker-Voirol et al. [1990a, b] vapor pressure data with the freezing points reported by Gable et al. [1950]. The ice line is also plotted for reference.
Figure 3.13 Sulfuric acid vapor pressures over partially frozen mixtures calculated from the Gibbs-Duhem equation and the freezing points reported by Gable et al. [1950] (solid curve). The dashed curve is obtained using the Jaecker-Voirol et al. [1990a, b] vapor pressure data.
solids; or a vapor, a liquid and a solid. Hence, in a plot of temperature vs. vapor pressure of one of the components the phase boundaries enclosing stability domains for the liquid or for the various hydrates can be represented as lines. The freezing envelopes are the boundaries between the stability domains for the liquid and solid phases. Vapor pressures and compositions of partially frozen equilibrium mixtures follow the freezing envelopes, a process that might continue at temperatures below the eutectic point (for example, 211 K for ice/hemihexahydrate) if the neighboring crystal phase does not nucleate, as noted below for the HCl/H₂O system.

The freezing envelopes inferred from our measurements are presented as solid curves in Figure 3.12, with the experimental points shown as open circles. For comparison, the freezing envelopes obtained by intersection of the vapor pressures reported by Jaecker-Voirol et al. [1990a, b] with the freezing points measured by Gable et al. [1950] are presented as dashed curves. As pointed out above, there is a significant discrepancy along the phase boundary of the ice/liquid mixture between the H₂O vapor pressures measured in our study (which are very close to those of pure ice) and the estimates based on the work of Jaecker-Voirol et al. [1990a, b], which yield much lower values.

Our calculated H₂SO₄ vapor pressures were also used to construct the freezing envelopes by intersecting sulfuric acid vapor pressures with the freezing points reported by Gable et al. [1950]. These results are given in Figure 3.13 (solid lines), along with those based on the data from Jaecker-Voirol et al. [1990a, b] (dotted lines).

Solids

80
Figure 3.14  Vapor pressures of water for solids in the \( \text{H}_2\text{SO}_4/\text{H}_2\text{O} \) binary system: +, tetrahydrate/dihydrate; □, ice/tetrahydrate or ice/octahydrate; \( \nabla \), ice/hemihexahydrate. The coexistence lines and the freezing envelopes are labeled. The dashed lines are for \( \text{H}_2\text{O} \) vapor pressures of liquid solutions. The solid line F-C-M represent a warming process at a \( \text{H}_2\text{O} \) partial pressure of \( 3.8 \times 10^{-4} \) Torr (corresponding to a mixing ratio of 5 ppmv at 100 mb, ~16 km altitude in the stratosphere). Point Q labels the quadruple point for \( \text{H}_2\text{SO}_4\cdot2\text{H}_2\text{O} \) and \( \text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O} \) coexisting with the gas and the liquid phases.
The solid-liquid phase diagram for the H$_2$SO$_4$/H$_2$O binary system was investigated by Gable et al. [1950] and by Vuillard [1957]. These authors identified five hydrates: mono-, di-, tri-, tetra-, and hexahydrate. Hornung et al. [1956] addressed the controversy related to the existence of another solid phase, the octahydrate; additionally, they suggested that the proper stoichiometry for the "hexahydrate" is 13:2, and hence, that it is actually an hemihexahydrate. Mootz and Merschenz-Quack [1987] further corroborated these findings by providing structural data from powder X-ray crystallography.

We carried out vapor pressure measurements of the solid crystals in the same manner as those for the liquids (except, of course, that the solids were not stirred). As expected, thermodynamic equilibrium between bulk solids required much longer times to be established: in most cases several hours. Water vapor pressures were measured for the coexistence systems of ice/octahydrate or ice/tetrahydrate, ice/hemihexahydrate, and tetrahydrate/dihydrate. These results are presented in Figure 3.14 as squares, triangles, and crosses, respectively. The freezing envelopes determined from our measurements are plotted as dotted curves. Also shown in this figure are the vapor pressures for liquid solutions (dashed lines).

The experimental water vapor pressures of the coexistence mixtures lie on straight lines when plotted as log $P_w$ vs. $1/T$. The scatter in the data about these lines is small (less than 5 %), indicating that equilibrium between the two solid compounds was effectively achieved. As expected, the H$_2$O vapor pressures over the coexistence mixtures of ice/tetrahydrate, ice/octahydrate, and ice/hemihexahydrate were very near those of pure ice (to within 5 %); the reason was discussed earlier. The results of a least squares fit of log $P_w = A - B/T$ for the di/tetrahydrate coexistence mixture are given also in Table 3.2.
As pointed out above, there is a unique relationship between the vapor pressure and the temperature for the equilibrium coexistence of two solid phases. Bulk solid mixtures often require a long time to reach equilibrium, but the use of small samples in some of the flow tube experiments facilitated this process (detailed descriptions of the apparatus are given in section 5.2). Experiments were performed using solutions with a H$_2$SO$_4$ concentration near that of the tetrahydrate: upon freezing, the solids exhibited initially H$_2$O vapor pressures very close to those of pure ice, characteristic of the coexistence mixture of ice/tetrahydrate. By slowly raising the temperature and by flowing dry helium over the samples, a sudden drop in the water vapor pressure was observed after some time, suggesting that the ice phase had evaporated, leaving only H$_2$SO$_4$$\cdot$4H$_2$O behind. The equilibrium H$_2$O vapor pressures over the substrate could then be regulated simply by addition or evaporation of small amounts of water, keeping the temperature constant; that is, the "H$_2$SO$_4$-rich" and "H$_2$O-rich" forms of the tetrahydrate could be generated by controlling the H$_2$O vapor pressure. The lowest values of this vapor pressure attained by evaporation agreed closely with those of the di/tetrahydrate coexistence mixture measured using bulk samples. As the temperature was raised over a period of 5 to 10 minutes, final melting was observed to occur at 243 K, which corresponds to the melting point of pure tetrahydrate. These results are qualitatively similar to those obtained earlier with the HNO$_3$/H$_2$O system, in agreement with the expectations based on phase equilibria considerations [Molina, 1993]. In the same manner, the hemihexahydrate was generated by freezing a solution with a 13:2 stoichiometric ratio (45.6 wt % H$_2$SO$_4$). As before, the H$_2$O vapor pressures initially attained were close to those of pure ice, indicating the formation of an ice/hydrate equilibrium mixture. H$_2$O vapor pressures smaller than those of pure ice could be obtained by evaporating
enough H₂O from this mixture to remove the ice phase, leaving the hydrate behind.

Samples with sulfuric acid concentrations greater than about 60 wt % would usually not crystallize upon cooling, as noted also by Gable et al. [1950]. These authors also reported that the trihydrate did not form these solutions unless seeded with trihydrate crystals, but the dihydrate or tetrahydrate formed instead. By repeated cooling and warming between 150 and 210 K we were able to freeze the 60 wt % solutions in the sample vessel utilized for vapor pressure measurements: crystallization occurred upon warming near 200 K. The solid began to melt at 226 K and hence consisted of an equilibrium mixture of tetra- and dihydrate, in agreement with the observations of Gable et al. [1950].

Melting of Sulfuric Acid Tetrahydrate

Some experiments were performed using the flow tube-mass spectrometer apparatus to investigate the melting behavior of solid H₂SO₄ aerosols in the stratosphere. H₂SO₄ tetrahydrate was first formed by freezing a 57.7 wt % H₂SO₄ solution. Subsequently, the temperature of the sample was slowly raised, keeping the H₂O partial pressure constant. As is represented by the line F-C-M in Figure 3.14, this process involves the transformation of H₂O-rich to H₂SO₄-rich hydrate, accompanied by only a minor change in the bulk composition of the hydrate. The sample was observed visually to melt at 218 K, corresponding to point M in Figure 3.14, which represents equilibrium between the tetrahydrate and the liquid at the particular H₂O partial pressure of the experiment. In principle, a solid-solid phase transition could have occurred at point C, the coexistence point between di- and tetrahydrate, if nuclei for the formation of the
dihydrate had been present; if so, the sample would not have started to melt at point M. This result is analogous to that involving freezing envelopes discussed earlier: a solid and a liquid phase can be in thermodynamic equilibrium with each other under conditions where both are metastable with respect to a different solid phase.

3.3.3 Infrared Spectra

Spectra of Liquid and supercooled liquid

Figure 3.15 shows spectra of various supercooled liquid sulfuric acid solutions near room temperature and in the 170 - 200 K range. The spectra consists mainly of two regions: strong, very broad absorptions at frequencies higher than 1500 cm\(^{-1}\) arising from H\(_2\)O and H\(_3\)O\(^+\) fundamentals, and somewhat narrower bands at lower frequencies, mostly from the sulfate group.

The bands in the spectra change slowly with temperature and composition, and at room temperature are in good agreement with those reported by Palmer and Williams [1975]. The spectra of the concentrated solutions undergo virtually no change in appearance with cooling, while for the more dilute solutions changes do occur. The changes are consistent with increased SO\(_4^{2-}\) at the expense of HSO\(_4^-\) upon cooling, by noting the band locations of SO\(_4^{2-}\) at 1104 and 613 cm\(^{-1}\) and HSO\(_4^-\) at 1341, 1230, 1050, 885 and 593 cm\(^{-1}\) summarized by Querry et al. [1974]. The increased ionization at lower temperatures was also observed in the Raman spectra of H\(_2\)SO\(_4\) solutions by Dawson et al. [1986] and by Kanno [1990]. The marked shifting of HSO\(_4^-\) \(\sim\) SO\(_4^{2-}\) results in the heat capacity change in a complicated way, as noted earlier.

Spectra of Crystalline Sulfuric Acid Hydrates

85
Figure 3.15 Infrared spectra of liquid $\text{H}_2\text{SO}_4$ solutions with compositions of 39, 43, 58, 65, and 73 wt % at temperatures near 300 and 190 K.
Figure 3.16 Spectra of crystalline hydrates $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. For $n = 1, 2,$ and 3 the spectra are presented at low temperatures (~140 K), showing sharper absorption bands. Spectra for $n = 4, 6.5,$ and 8 change relatively little with temperature and are shown at 195 K.
Figure 3.17 Evolution of infrared spectra of a 47.6 wt % H$_2$SO$_4$ solutions with temperatures. Crystallization of H$_2$SO$_4$$\cdot$6.5H$_2$O occurs between 190 and 200 K upon cooling. No significant changes occur upon warming to 210 K. The hemihexahydrate converts into tetrahydrate plus liquid at around 220 K. The tetrahydrate melts by 233 K.
TABLE 3.4. Frequencies (cm\(^{-1}\)) of major infrared bands of crystalline hydrates of H\(_2\)SO\(_4\) sampled at 143 ± 10 K.

<table>
<thead>
<tr>
<th>H(_2)SO(_4)•H(_2)O</th>
<th>H(_2)SO(_4)•2H(_2)O</th>
<th>H(_2)SO(_4)•3H(_2)O</th>
<th>H(_2)SO(_4)•4H(_2)O</th>
<th>H(_2)SO(_4)•6.5H(_2)O</th>
<th>H(_2)SO(_4)•8H(_2)O</th>
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<tr>
<td>2260–2100</td>
<td>2250</td>
<td>2250</td>
<td>2450–2250</td>
<td></td>
<td>2420–2200</td>
</tr>
<tr>
<td>1785</td>
<td>1925</td>
<td>1616</td>
<td>1690</td>
<td>1950–1650</td>
<td></td>
</tr>
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<td>1725</td>
<td>1775</td>
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<tr>
<td>1198</td>
<td>1204</td>
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Figure 3.16 shows the infrared spectra for various H$_2$SO$_4$ hydrates. Table 3.4 summarizes the frequencies of major infrared bands of these crystalline hydrates at temperatures around 140 K. Figure 3.17 illustrates the changes observed in the infrared spectra of a 47.6 wt % solution with temperature, showing the crystallization to form hemihexahydrate between 190 and 200 K, and the subsequent peritectic transition at 219 K to form the tetrahydrate, and melting at about 233 K. In general, for the pure crystalline hydrates, the melting points as well as phase transition temperatures agreed very well with those found in the thermal analysis and vapor pressure measurements.

Next, we discuss the spectra for each of the hydrates:

(a) Monohydrate. Our spectrum agrees very well with that reported by Savoie and Giguère [1964] within the resolution and wavenumber accuracy of the earlier, non-FTIR work. The lack of symmetry of the bisulfate ion in the crystal [Taesler and Olovsson, 1968] is consistent with the multitude of peaks in the spectrum, including the appearance of the sharp peak(s) in the 950-990 cm$^{-1}$ range probably due to the symmetric sulfate $\nu_1$ stretch [Dawson et al., 1986], which is infrared forbidden in a fully symmetric environment.

(b) Dihydrate. The spectrum reported by Giguère and Savoie [1960] for the dihydrate is noticeably different from our crystalline spectrum, but is similar to that of a supercooled film. Their sampling method was similar to ours, but, because of the lack of change in the bands, they expressed some doubt as to whether crystallization had indeed occurred. For genuinely crystalline samples the x-ray structure [Taesler and Olovsson, 1969] and Raman spectrum [Millen and Vaal, 1956] show complete ionization, (H$_3$O$^+$)$_2$SO$_4^{2-}$. In an isotropic environment the symmetric SO$_4^{2-}$ group would have few observable infrared vibrations, but this crystal has two independent types
of sulfate groups, neither of which are fully symmetric. Consequently, the complexity of the infrared spectrum here is also consistent with the reported structure.

(c) Trihydrate. No published structure or spectra are available for comparison, but the complexity of the spectrum indicates a low symmetry for the sulfate anion.

(d) Tetrahydrate. As with the dihydrate, the spectrum from Giguère and Savoie [1960] strongly resembles that of a noncrystalline film, which is again noticeably different from the crystalline spectrum presented here. The spectrum consists of the broad $\text{H}_3\text{O}^+$ bands at higher frequencies and just two dominant $\text{SO}_4^{2-}$ bands near 1077 and 600 cm$^{-1}$ (for comparison, $\text{SO}_4^{2-}$ in dilute potassium sulfate solution has active bands at 1104 and 613 cm$^{-1}$, according to Querry et al., [1974]). This is consistent with the high symmetry of the ion in the crystal structure report [Kjällman and Olovsson, 1972].

(e) Hemihexahydrate. Our results are consistent with the crystal structure report [Mootz and Merschenz-Quack, 1987], in that they showed a slightly distorted $\text{SO}_4^{2-}$ ion with S-O distances nearly equal to those in the tetrahydrate. We also observed that around 220 K the hemihexahydrate converted into tetrahydrate plus some liquid (Figure 3.17), consistent with the DSC and vapor pressure measurements.

(f) Octahydrate. For this hydrate, the sulfate stretching region strongly resembles that of the tetrahydrate, which is reasonable considering the similarity of the reported site symmetries and bond lengths for the $\text{SO}_4^{2-}$ ion in both crystals [Mootz and Merschenz-Quack, 1987]. The spectral similarities, however, make differentiation between the pure octahydrate and a tetrahydrate/ice mixture difficult and hence there is some uncertainty in its identification. Here, the changes as the temperature is raised above the phase transition temperature do not lead to an unambiguous
confirmation, because of the proximity of the octahydrate to hemihexahydrate transition at 201 K and the extrapolated ice-tetrahydrate metastable eutectic at 200 K [Giauque et al., 1960].

3.3.4 Calorimetric Measurements

Extensive DSC experiments were performed in this study, with a H$_2$SO$_4$ content ranging from 0 to 75 wt %, in order to investigate the nature of the phase diagram of H$_2$SO$_4$/H$_2$O binary system and to establish the identity of various hydrates.

Figure 3.18 shows DSC warming curves of selected frozen sulfuric acid mixtures. The results show that the frozen sample of 20 wt % (middle curve) consists initially of a mixture of ice and octahydrate, and that this hydrate transforms into the hemihexahydrate at 200 K. Upon further warming, the hemihexahydrate melts at its eutectic with ice, 211 K, leaving ice and liquid. The last of ice melts at about 259 K. The frozen sulfuric acid solution of 50 wt % (bottom curve) also consists initially a mixture of octahydrate and tetrahydrate; again, the octahydrate transforms into H$_2$SO$_4$·6.5H$_2$O at 200 K. However, the hemihexahydrate does not melt in this case; it undergoes a peritectic transition at 219 K to form the tetrahydrate. The sample with a content of 40 wt % (top curve) yields a coexistence mixture of ice and hemihexahydrate, with an eutectic point at 211 K and a final melting point around 217 K.

Additional results of DSC experiments are given in Figure 3.19, which presents both cooling and warming curves for frozen 35.8, 37.6, 57.7, 64.5, and 73.2 wt % H$_2$SO$_4$ mixtures. The 35.8 (Figure 3.19 (a)) and 37.6 (Figure 3.19 (b)) samples correspond to the eutectic mixtures of ice/hemihexahydrate and ice/tetrahydrate, and have melting temperatures at 211 and
Figure 3.18 DSC warming curves showing hydrate meltings. The peaks near 200 K represent either the eutectic meltings of ice/tetrahydrate followed by crystallization into hemihexahydrate, or the solid to solid conversion of octahydrate into hemihexahydrate. The coexistence mixtures of ice/hemihexahydrate melt near 211 K. For the 50 wt % H$_2$SO$_4$ frozen mixture, the H$_2$SO$_4$·6.5H$_2$O undergoes a peritectic reaction at 219 K to form H$_2$SO$_4$·4H$_2$O. For the 20 wt % H$_2$SO$_4$ frozen mixture, the warmest peak corresponds the melting of ice. Weight percentages of H$_2$SO$_4$ are labeled in the figure.
Figure 3.19  More DSC cooling and warming curves of various H_2SO_4 solutions.
200 K, consistent with the eutectic points of these two coexistence mixtures. For the frozen
tetrahydrate (57.7 wt %, Figure 3.19 (c)) solution, only single melting peak exists at 241 K, the
melting point of pure tetrahydrate. The solution with the trihydrate composition was never
crystallized (Figure 3.19 (d)).

For frozen mixtures less than 35.8 wt %, the phase transitions near 200 K resemble those
of the 20 wt % solution, but with different temperatures for the final ice melting, whereas for
frozen mixtures of 50-57 wt % the phase transition temperatures are essentially the same as the
50 wt % solution at low temperatures, except for the final SAT melting temperatures.

The phase transitions in Figures 3.17 and 3.18 correspond closely to those in the H₂SO₄
phase diagram reported by Giauque et al. [1960]. These results along with various other
calorimetric measurements performed in our laboratory are in excellent agreement with the
findings of Giauque et al. [1960] and Mootz and Merschenz-Quack [1987] in terms of
establishing the nature of the phase diagram and the identity of the various hydrates.

Enthalpies of fusion for H₂SO₄ hydrates have been previously investigated by Rubin and
and tetrahydrate, and by Hornung et al. [1956] for hemihexahydrate, and have recently been
collaborated by Zeleznik [1991]. As a result, they were not examined in details in this work. An
example of such measurements is given in Figure 3.19 (c), in which the transition energy for the
melting of tetrahydrate is measured to be 170.67 J/g, consistent with the literature value (169.6
J/g) [Zeleznik, 1991].

3.3.5 Freezing, Supercooling, and Glass Transition Temperatures
Some preliminary information on supercooling and freezing of the H₂SO₄/H₂O solutions was obtained from the calorimetric, conductivity, and mass spectrometer measurements. More systematic studies on supercooling of the H₂SO₄ solutions were carried out by Beyer [1993], and were reported by Molina et al. [1993].

The results indicate that supercooling for less concentrated solutions (< 35 wt %) appears difficult: ice precipitates out shortly upon reaching its equilibrium freezing temperatures; subsequently, the hydrate crystallizes at temperatures between 180 and 190 K. Supercooled solutions of 45-57 wt % would freeze at temperatures near 190 K. More concentrated solutions (greater than 57.8 wt %) supercool readily, even if being left at low temperatures for hours (between 190 and 220 K). It was also found that solutions with contents between 35.6 and 45.2 wt % exhibit no crystallization upon cooling in the DSC experiments, but these solutions crystallize upon warming to ~ 170-190 K. The mass spectrometer measurements, on the other hand, indicated that these solutions do freeze at temperatures between 180 and 190 K upon cooling. The difference between the DSC and mass spectrometer measurements is understandable, in light of the different amounts of solution used in both experiments: the sample with the larger volume used in the mass spectrometer experiments has a higher probability of containing nucleation sites or freezing nuclei and, therefore, is more likely to freeze. Alternatively, the slow cooling rate in the mass spectrometer observations may also facilitate freezing.

Also, as shown in Figure 3.19 (d), if a solution does not crystallize at low temperatures, glasses with arbitrary compositions may form. The glass transition temperatures (T_g) rise slightly with increasing H₂SO₄ concentration, i.e., T_g = 150 K for a 35.8 wt % solution and T_g = 173
K for the 73.2 wt % solution. These results are in very good agreement with the observations of Vuillard [1957].

3.3.6 Stratospheric Implications

Sulfuric acid aerosols are hygroscopic, and are essentially in equilibrium with water vapor in the stratosphere which is present at several ppm. In contrast, equilibrium with respect to \( \text{H}_2\text{SO}_4 \) vapor is less likely to be attained because of the exceedingly low concentrations of this vapor [Möhler and Arnold, 1992]. Equilibrium with water vapor implies that the stratospheric aerosol particles deliquesce as the temperature decreases. Steele et al. [1983] estimated sulfuric acid concentrations as a function of temperature for a given ambient \( \text{H}_2\text{O} \) partial pressure, using the \( \text{H}_2\text{O} \) vapor pressure data taken from Gmitro and Vermeulen [1964]; their results are shown in Figure 3.20, together with the estimates based on the data of Jaecker-Voirol et al., [1990a, b] and with those based on our vapor pressure measurements. There is a significant disagreement between the curve estimated from the Jaecker-Voirol et al. data and the other two curves, as expected from our discussion in the "Vapor pressure measurements" section. Note, also, that below 200 K the aerosols contain significant amounts of nitric acid, which affect the \( \text{H}_2\text{SO}_4 \) concentrations.

Figure 3.20 also shows freezing envelopes; as can be seen in the figure, the \( \text{H}_2\text{SO}_4 \) aerosols are supercooled for the conditions represented by the solid lines, and are expected to be supercooled throughout most of the stratosphere. Atmospheric observations indicate that the bulk of the sulfate particles in the stratosphere are indeed in the liquid phase [Turco et al., 1982; Dye
Figure 3.20 Equilibrium sulfuric acid compositions of background stratospheric aerosols as a function of temperature and H$_2$O mixing ratios at 100 mb (~16 km altitude), as estimated from different vapor pressure data: the solid lines are based on data from this work (a, 5 ppmv; b, 3 ppmv H$_2$O); the dashed line is based on data of Jaecker-Voiorl et al. [1990a, b] (5 ppmv H$_2$O); the dashed-dotted line is from the results of Steele et al. [1983] (5 ppmv H$_2$O). Also shown in this figure is the freezing envelop of sulfuric acid solutions [Gable et al., 1950]. Points F and M label the corresponding freezing and melting points.
et al., 1992; Pueschel et al., 1992; Toon et al., 1993]. Supercooling experiments in our laboratory also indicate that the sulfate aerosols are not likely to freeze unless the temperature drops below ~ 200 K [Molina et al., 1993].

If the temperature drops sufficiently the aerosols may crystallize to form $\text{H}_2\text{SO}_4$ hemihexahydrate and/or tetrahydrate, together with $\text{HNO}_3$ trihydrate (NAT), to be discussed in section 4.4. If the temperature reaches the frost point, ice may form as well (points $F_s$ and $F_h$ in Figure 3.20).

The situation with respect to the melting of frozen aerosols can be reasonably defined: once crystallized, the hydrates are stable until they either melt or evaporate. These are the processes for which the equivalent of supercooling does not occur, and hence, their occurrence can be predicted reliably using thermodynamic considerations. Consider, for example, a PSC particle consisting of NAT with a core of $\text{H}_2\text{SO}_4$ hemihexahydrate, in a region of the stratosphere that is warming. Above the saturation temperature with respect to NAT the bulk of the particle evaporates, leaving behind the hemihexahydrate; no melting occurs at this stage. This temperature is typically around 195-197 K, depending on the ambient partial pressures of $\text{HNO}_3$ and $\text{H}_2\text{O}$. Inspection of Figure 3.20 may lead, at first sight, to the conclusion that once frozen the sulfuric acid particle never melts in the stratosphere, because the temperatures characteristic of the region of stability of the liquid are not reached. However, this conclusion implies that solid-solid phase transformations do take place as the temperature increases. Our experiments show that indeed the hemihexahydrate as well as the octahydrate transform readily into the tetrahydrate, without melting. This process is likely to occur in the stratosphere as well, and would be accompanied by evaporation of water. In contrast, our observations reveal that the
tetrahydrate does not transform into any of the lower hydrates; instead it melts at a temperature at which it is in equilibrium with the liquid solution having a $\text{H}_2\text{O}$ vapor pressure equal to the ambient $\text{H}_2\text{O}$ partial pressure, typically around 215 K (point M in Figure 3.14 or points $M_s$ and $M_b$ in Figure 3.20). As melting occurs, water evaporates, because the liquid is more concentrated in $\text{H}_2\text{SO}_4$ than the tetrahydrate. Above this melting temperature the liquid phase is stable with respect to the tetrahydrate, although it is metastable with respect to the tri- and dihydrate. These two hydrates happen to be difficult to generate merely by cooling liquid solutions; they usually crystallize only after cooling below 150 K to form a glass, and after subsequent rewarming. As the temperature increases in the stratosphere the acid concentration increases, and at some point the liquid becomes metastable with respect to the monohydrate. However, crystallization of the sulfuric acid droplets does not appear to occur in the stratosphere at such temperatures, as inferred from atmospheric observations [Turco et al., 1982; Dye et al., 1992; Pueschel et al., 1992; Toon et al., 1993].

It should be pointed out, though, that sedimentation of ice crystals in late winter over Antarctica may remove a significant fraction of the frozen sulfate aerosols from the stratosphere, by scavenging [Goodman et al., 1989] and by acting as condensation nuclei in the formation of PSCs [Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990; Molina et al., 1993].

3.4 The HCl/H$_2$O Binary System

3.4.1 Introduction
As mentioned in chapter one (i.e., equations (1.10) and (1.12)), the availability of HCl on the PSC particles is an essential issue for the heterogeneous chemistry.

Historically, Pickering [1893], Rupert [1909], and Vuillard [1955, 1957] measured freezing points of HCl solutions and identified several crystal hydrates: the mono-, di-, tri-, and hexahydrate. The measurements of Vuillard [1957] made by differential thermal analysis are probably the most extensive to date, giving information on freezing points of HCl solutions as well as transition temperatures for supercooled HCl solutions to glass.

The interaction of HCl with ice and NAT films representative of PSCs has been recently investigated using FTIR [Abbatt et al., 1992; Koehler et al., 1993]. Infrared spectra of HCl hydrates were also reported [Gilbert and Sheppard, 1973; Ritzhaupt and Devlin, 1991].

Some discrepancies exist in solubility and partition coefficient measurements for water ice. Molina et al. [1987] found that HCl had a large affinity for ice at temperatures as low as 185 K and suggested that HCl might be dissolved in bulk ice; in later work, it became clear that the HCl uptake is mainly confined to the ice surface [Abbatt et al., 1992]. Wofsy et al. [1988] reported that the solid-liquid partition coefficient is near constant, with values apparently increasing from 0.25 to 0.3 as the HCl concentration increases from 0.05 to 0.14 mole fraction. By using the observed partition coefficients to calculate the partial molar enthalpy of vaporization for HCl from ice, they estimated the HCl content of ice that forms in the stratosphere would be on the order of a few mol %.

However, Seidensticker [1972], Gross et al. [1975], and Gross et al. [1987] noted the difficulty in growing single-crystal ice at higher HCl concentrations and lower temperatures. They postulated that a solubility limit for HCl in single crystal ice is of about 0.0008 mole
fraction. Similarly, Wolff et al. [1989] showed that HCl is not easily incorporated into ice crystals at low temperatures, with an upper limit of partition coefficient about 0.002.

Hansen and Mauersberger [1988c, 1990] measured vapor pressures for the H$_2$O/HNO$_3$/HCl ternary system for temperatures down to 180 K. They reported that the solubility of HCl in ice is low, less than 0.01 mole fraction for stratospheric conditions, but NAT crystals exhibit much greater ability to absorb HCl than does pure ice for HCl pressures characteristic of the stratosphere. Also, they concluded that HCl does not act like a strong electrolyte in pure ice, but HCl is fully dissociated in NAT. Marti et al. [1991] also reached the similar conclusions.

As noted above, it has been recently realized that the availability of HCl at the surfaces of PSC particles, rather than bulk solubility, is what matters for the heterogeneous reactions [Molina, 1993], as indicated by HCl uptake experiments to be discussed in section 5.3.2.

In this section, we report experiments to explore physical chemistry of the HCl/H$_2$O binary system.

3.4.2 Thermal Analysis and Electrical Conductivity

Experiments were performed by recording electrical conductivity as a function of temperature, by using differential thermal analysis (DTA) and differential scanning calorimetry (DSC) for samples consisting of aqueous solutions in the range from 0 to about 30 % weight HCl.

Figure 3.21 shows DSC warming curves of selected HCl solutions. Additional results of
the DSC experiments are given in Figure 22. The 25 wt % solution corresponds to the pure hexahydrate composition, whereas the 23 wt % and 26.6 wt % solutions correspond to the eutectic mixtures of ice/hexahydrate and tri-/hexahydrate.

Results of the freezing point measurements reveal that liquids with a composition in the range from 20 wt % to 25 wt % supercool readily and freeze only below about 170 K. The hexahydrate does not form by freezing the liquid, but it forms by cooling the samples below \( \sim 150 \) K and by rewarming. Melting of the hexahydrate occurs at about 200 K. For more concentrated solutions, the trihydrate crystallizes directly from the liquid; the ice-trihydrate eutectic occurs at 186 K for a composition of 25%. There is a glass transition temperature around 138 K, and the crystallization of the glass occurs upon rewarming at about 150 K and is accompanied by a large release of heat. These results are in very good agreement with those reported earlier by Vuillard [1955, 1957].

Another set of experiments was carried out with samples prepared by deposition of HCl vapor at partial pressures in the range from \( 10^{-5} \) Torr to \( 10^{-4} \) torr and at temperatures between 178 and 198 K on ice crystals of powder ice (consisting of micron-sized ice particles, details given in section 5.4). Within experimental error, the results are the same as those obtained with samples prepared by mixing an aqueous solution of approximately 20% weight HCl with the ice particles at 220 K (just above the freezing point of the solution), in amounts such as to yield samples with an overall composition of about 0.01 to 0.5 wt % HCl. Also, the same results are obtained by freezing 0 to 5 wt % HCl solutions prepared at room temperature, which yields much larger ice crystals. Indeed, samples prepared by those various methods correspond to the ice/liquid coexistence mixture so that the composition change of the remaining HCl liquid with
Figure 3.21 DSC warming curves of various HCl solutions. The negative peaks around -80°C indicate crystallization, which is accompanied by a heat release. The peaks near -70°C correspond to melting of HCl hexahydrate, and the peaks above -20°C represent melting of the HCl-doped ice, which is absent for the 25 wt % solution. The heating rates are 4°C/min for the 25 and the 11 wt % solution, and 10°C/min for the 2 wt % solution.
Figure 3.22  DSC warming curves for 23 and 26.6 wt % HCl solutions.
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decreasing temperature follows the freezing envelope given by Wofsy et al. [1988] until glass formation at 133 K, consistent with the findings of Vuillard [1957]. It is also clear that HCl hexahydrate is formed in most of these samples if they are cooled below 150 K, as evidenced in the warming curves by the melting point of the hydrate at about 200 K (see Figure 3.21).

Our results imply that in order to form hexahydrate by freezing aqueous HCl solutions certain hexahydrate nuclei must be present. These nuclei probably carry the same molecular structure as that of hexahydrate and can be produced by cooling HCl solutions to lower temperatures (below 150 K). In one case, we first cooled a 25 wt % HCl solution to 150 K and then warmed it up. Following complete melting at 200 K, the sample was kept at 210 K for at least 10 minutes and then recooled. The hexahydrate was observed to form at 185 K upon cooling, suggesting that the hexahydrate nuclei are capable of surviving melting. Koehler et al. [1993] also noted difficulty in growing hexahydrate film in their experiments and suggested that nucleation of crystalline of HCl hexahydrate may not be facile in the stratosphere.

No measurements of heats of fusion for the HCl binary system were reported previously. The present data obtained from the DSC include those for the pure hexahydrate (Figure 3.21) and for ice/hexahydrate and tri/hexahydrate coexistence mixtures (Figure 3.22), summarized in Table 3.5.

3.4.3 Vapor Pressures

Direct measurements of vapor pressures over the HCl/H$_2$O binary system are rather limited. In fact, Hanson and Mauersberger [1988c, 1990] were only able to measure the HCl
Figure 3.23 HCl vapor pressures of the HCl/H$_2$O binary system: Δ, liquid/solid; +, ice/hexahydrate. The long dashed lines are vapor pressures of liquid HCl solutions extrapolated from the data of Fritz and Fuget [1956]. The tri/hexahydrate coexistence line is taken from the data of Hanson and Mauersberger [1990]. The short dashed lines are the freezing envelope.
vapor pressures of pure trihydrate and the trihydrate/hexahydrate coexistence curves. The ice/hexahydrate coexistence curve was extrapolated utilizing the freezing point curves by Vuillard [1955] and their own liquid vapor pressure data, since they noted difficulty in growing hexahydrate by temperature cycling a vapor-deposited 6:1 H₂O/HCl mixture or through establishing the coexistence of the hexahydrate with ice by manipulating partial pressures.

The vapor pressures of HCl/ice samples prepared in various ways were measured with the mass spectrometer in the temperature range from 183 to 213 K, using the static technique. Figure 3.23 shows the results for samples prepared by freezing aqueous solutions with 0.1, 1.0, and 17.5 wt % HCl weight (open triangle); at the investigated temperatures these samples consist of an equilibrium mixture of a liquid HCl solution with ice and the vapor pressure versus temperatures line represents the solid-liquid coexistence conditions.

Samples were also prepared by depositing HCl vapor at partial pressures in the range from 10⁻⁵ torr to 10⁻⁴ torr and at temperatures between 178 and 198 K on ice crystals. These samples had final compositions between 0.05 and 0.1 wt % HCl. The substrate was either powder ice or ice prepared by condensation of water vapor on the glass surface of the sampling tube at about 198 K. In addition, samples were prepared by mixing at 220 K liquid solutions of about 20 wt % HCl with powder ice to yield overall compositions of 0.1, 0.5, and 2 wt % HCl. Within experimental error the results of the vapor pressure measurements for all these samples were indistinguishable from those measured for samples prepared by freezing liquid solutions, i.e., the vapor pressures fall on the freezing envelope.

The vapor pressure measurements were reproducible as the temperature was raised or lowered down to 183 K. However, if the samples were cooled to below 150 K (and in some
cases, to only 170 K) and then rewarmed, the resultant HCl vapor pressures decreased relative to those of the samples cooled to only 183 K. Clearly, at the lower temperatures the liquid phase froze, yielding a new solid phase in the form of HCl•6H₂O. HCl vapor pressures over the ice/hexahydrate coexistence are shown as crosses in Figure 3.23, along with the tri/hexahydrate coexistence line reported by Hanson and Mauersberger [1990].

3.5 The HNO₃/H₂O Binary System

3.5.1 Introduction

Due to its direct relevance to PSCs, the HNO₃/H₂O binary system has recently been extensively investigated.

Historically, Pickering [1893] and Kuster and Kremann [1904] measured freezing temperatures for a wide range of HNO₃ concentrations. Those studies also identified the formation of mono- and trihydrate as well as the presence of solid ice for low HNO₃ concentrations and solid HNO₃ for high concentrations. Petit and Ji [1991] have recently expanded the HNO₃/H₂O phase diagram by including the dihydrate.

Vapor pressures of the HNO₃/H₂O binary system were originally investigated by Hanson and Mauersberger [1988a]. New vapor pressure measurements [Worsnop et al., 1993] have confirmed that PSCs consisting of NAT crystals may form at temperatures several degrees above the ice frost point, in support of the previous finding of Hanson and Mauersberger [1988a]. The new measurements have also included thermodynamic data for HNO₃•2H₂O (NAD) and a higher hydrate (HNO₃•10H₂O).
Ritzhaulpt and Devlin [1991], Tolbert and Middlebrook [1990], and Smith et al. [1991] have measured infrared spectra of thin films of condensed HNO₃/H₂O mixtures, including mono-, di-, and trihydrate. In addition, Koehler et al. [1992] suggested two possible forms of NAT: an α-NAT formed at colder temperatures and a β-NAT formed at warmer temperatures. Infrared spectra of small NAT and NAD aerosol particles have also been reported [Barton et al., 1993].

In this section, we only present measurements made by the DSC. Thermodynamic properties and some vapor pressure measurements of this system are to be discussed in section 3.6 and 5.2.4, respectively.

3.5.2 Thermal Analysis

Extensive DSC experiments were performed in order to study the HNO₃/H₂O phase diagram, freezing and supercooling, and heats of fusion for pure HNO₃ crystalline hydrates as well as some eutectic mixtures.

Results of the DSC cooling and warming runs are shown in Figure 3.24. The 32.5 and 70 wt % solutions correspond to the ice/NAT and NAT/NAM eutectic mixtures, whereas the 53.8 and 63.3 wt % solutions correspond to pure NAT and NAD compositions. As is seen from this figure, for dilute solutions (≤ 32.5 wt %), ice precipitates out at warmer temperatures followed by crystallization of NAT; more concentrated solutions (> 32.5 wt %) freeze at temperatures between 190 and 220 K. Note that, unlike HCl or H₂SO₄ solutions, HNO₃ solutions with compositions from 0 to 70 wt % would be completely frozen upon cooling below 190 K.

Heats of fusion were measured for pure NAT and NAD compositions as well as for the
Figure 3.24 DSC cooling and warming curves of various HNO₃ solutions. The 53.4 and 63.4 wt % solutions correspond to the NAT and NAD compositions, whereas the 32.5 and 70 wt % solutions correspond to the ice/NAT and NAT/NAM eutectic mixtures.
Figure 3.25 Evolution of infrared spectra with temperature for a frozen 63.4 wt % HNO₃ solution.
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<th>Melting Point (K)</th>
<th>$\Delta H_{fus}$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$·2H$_2$O</td>
<td>238</td>
<td>228.28</td>
</tr>
<tr>
<td>HNO$_3$·3H$_2$O</td>
<td>254.6</td>
<td>246.80</td>
</tr>
<tr>
<td>Ice/NAT</td>
<td>233.5</td>
<td>217.96</td>
</tr>
<tr>
<td>NAT/NAM</td>
<td>227.7</td>
<td>198.05</td>
</tr>
</tbody>
</table>
ice/NAT and NAT/NAD eutectic mixtures, summarized in Table 3.6. For NAT (Figure 3.24 (c)), the measurement yields a value of 28.9 kJ/mole, consistent with the value of 29.1 kJ/mole reported by Forsythe and Giauque [1942]. Also, as shown in Figure 3.24 (d), we measured the heat of taking solid NAD at 232 K to liquid solution at 245 K to be 22.6 kJ/mole, although it is likely that this heat is the combined heat of the peritectic melting of NAD to solution and NAT and of warming and melting the NAT and solution until no NAT remains. Our DSC results for NAD appear consistent with those recently reported by Petit and Ji [1991], who identified the NAD formation using the so called Tamman diagram, which is based on a plot of the heat of phase change against the HNO₃ concentration.

Support for the presence of NAD in the calorimetry cell, rather than a NAT/NAM mixture, comes also from parallel experiments wherein samples of liquid HNO₃•2H₂O solution were held between sapphire or AgCl windows and cooled and rewarmed [Wooldridge et al., 1993]. As shown in Figure 3.25, the infrared spectra indicate the spontaneous formation of NAD from the liquid upon cooling, and the conversion of NAD to liquid/NAT on warming through the 220-230 K range, followed by the complete melting of NAT by ~245 K. Our spectra compare well with those for NAD reported by Ritzhaupt and Devlin [1991] and for NAD and β-NAT by Koehler et al. [1992]. In addition, the bands in the 2400-2700 cm⁻¹ region arising from the incorporation of ~2% heavy water in the sample solutions aid in the identification of the NAD to NAT transition.

It is also interesting to note that the heats of fusion for NAM, NAD, and NAT increase in that order. Furthermore, the differences in the heats between NAD and NAM and between NAT and NAD are about 6 kJ/mole, which is essentially equal to the heat of fusion for pure ice.
A similar behavior can also be identified among some hydrates of sulfuric acid (Table 3.8).

3.6 Thermodynamics and Phase Equilibria of Binary Acid Systems: Theoretical Considerations

3.6.1 Introduction

As discussed earlier in this chapter, many experimental studies have been carried out to study physical chemistry of the H₂SO₄/H₂O, HNO₃/H₂O, and HCl/H₂O binary systems at low temperatures, because of their reverence to the stratospheric chemistry. Thermodynamic data from various sources have recently been correlated and parameterized for the H₂SO₄/H₂O system by Zeleznik [1991] and for HNO₃/H₂O system by Clegg and Brimblecombe [1990]. Theoretical predictions for vapor pressures of those systems have also been reported by Jacker-Voirol et al. [1990a, b]. In addition, Smith [1990] discussed gas-solid equilibria and the formation of HNO₃ hydrates in terms of chemical equilibrium principles.

In this section, thermodynamic properties and phase equilibria are investigated for the HCl/H₂O, HNO₃/H₂O, and H₂SO₄/H₂O binary systems. Standard enthalpies of formation for pure crystalline hydrates as well as their corresponding liquid compositions are obtained using thermodynamic data from this study and from the literature. We also present a theoretical approach to determine thermodynamic equilibrium for two adjunct hydrates and for the coexistence systems involving a hydrate and ice.

3.6.2 Methodology
The important parameters in describing chemical equilibrium of various phases are enthalpies and enthalpy changes for each of the substances and reactions in consideration. Consider the following generalized chemical reaction

\[ \sum_{i=1}^{N} v_i M_i = 0 \]  

(3.7)

in which \( M_i \) are the components and \( v_i \) define the stoichiometry [see, e.g., Denbigh, 1981]. The condition for chemical equilibrium is the balancing of chemical potentials

\[ \sum_{i=1}^{N} v_i \mu_i = 0 \]  

(3.8)

The equilibrium constant involving the partial pressures, \( P_i \), is defined as

\[ K_p = \prod_{i=1}^{N} P_i^{v_i} \]  

(3.9)

At the conditions of interest all vapors will be present at \( P_i < 1 \) atm and so are safely treated as ideal gases. Thus, using the relation

\[ \mu_i = \mu_i^0(T) + RT \ln P_i \]  

(3.10)
equations (3.7) to (3.9) become

\[ -RT \ln K_p = \sum_{i=1}^{N} v_i \mu_i^0 \]  

(3.11)

For a single condensed phase in equilibrium with the vapor in a binary system, equation (3.7) becomes,

\[ v_A A(g) + v_B B(g) \rightleftharpoons C(s), \quad \Delta H_{\text{subl}}^0 \]  

(3.12)
where $\Delta H_{\text{subl}}^0$ is the enthalpy change upon sublimation. Considering first the temperature dependence of $K_p$, we have

$$-R \frac{\partial \ln K_p}{\partial T} = \left[ \frac{\partial (\mu^0_{C(s)}/T)}{\partial T} - \nu_A \frac{\partial (\mu^0_{A(g)}/T)}{\partial T} - \nu_B \frac{\partial (\mu^0_{B(g)}/T)}{\partial T} \right]$$

(3.13)

which with a Gibbs-Helmholtz relation

$$\frac{\partial (\mu^0_i/T)}{\partial T} \Bigg|_p = -\frac{H^0_i}{T^2} \quad \text{or} \quad \frac{\partial \mu^0_i}{\partial (1/T)} \Bigg|_p = -H^0_i$$

(3.14)

becomes

$$RT^2 \frac{\partial \ln K_p}{\partial T} = R \frac{\partial \ln K_p}{\partial (1/T)} = \nu_A H^0_{f,A(g)} + \nu_B H^0_{f,B(g)} - H^0_{f,C(s)} = \Delta H^0_{\text{subl}}$$

(3.15)

where the $H^0_{f,i}$'s are the standard enthalpies of formation. The entropy changes, i.e., the intercepts of the following equation, are found in a similar manner,

$$R \ln K_p = \Delta S^0_{\text{subl}} - \Delta H^0_{\text{subl}}/T$$

(3.16)

Enthalpies of formation for individual crystalline hydrates can be derived by considering the following reactions

$$\nu_A A(l) + \nu_B B(l) \rightleftharpoons C(l), \quad \Delta H^0_{\text{mix}}$$

(3.17)

$$C(l) \rightleftharpoons C(s), \quad \Delta H_{\text{fus}}$$

(3.18)

On combining equations (3.12), (3.17), and (3.18), we have

$$H^0_{f,C(s)} = \nu_A H^0_{f,A(l)} + \nu_B H^0_{f,B(l)} + \Delta H^0_{\text{mix}} + \int C_p(T)dT + \Delta H_{\text{fus}} + \int C_p(T)dT$$

$$298 \quad 298$$

$$T_{\text{fus}}$$

(3.19)

In this equation, adjustment of the thermodynamic values to 200 K has been made using heat capacity data.
Values for $H^0_i$’s and $S^0_i$’s for the pure liquid components at 298.15 K are given in standard compilations of thermodynamic data such as the CRC Handbook [Lide, 1993], Perry’s Chemical Engineers’ Handbook [Perry, 1984], the JANAF Tables [Chase et al., 1985], Lange’s Handbook [Dean, 1992], etc.; and sometimes directly for the hydrates as well, such as for sulfuric acid.

Now we consider the situation when two hydrates are in equilibrium with the vapor. We begin with equation (3.12) for one hydrate and introduce

$$v'_A A(g) + v'_B B(g) \leftrightarrow C'(s), \quad \Delta H^0_{\text{subl}}$$

for the other. As the partial pressure of $B$ ($P_B$) over $C$ and $C'$ are equal, the pair of equations (3.9) for the $K_p$ of $C$ and $C'$ are combined to eliminate $P_B$, yielding

$$\left(\frac{v_A}{v_B} - \frac{v'_A}{v'_B}\right) \ln P_A = \frac{1}{v_B} \ln K_p - \frac{1}{v_B}$$

with a temperature dependence

$$-RT^2 \left(\frac{v_A}{v_B} - \frac{v'_A}{v'_B}\right) \frac{\partial \ln P_A}{\partial T} = \frac{1}{v_B} \left[H^0_{f,C(s)} - v_A H^0_{f,A(g)} - v_B H^0_{f,B(g)}\right] - \frac{1}{v'_B} \left[H^0_{f,C'(s)} - v'_A H^0_{f,A(g)} - v'_B H^0_{f,B(g)}\right]$$

or equivalently

$$\frac{\partial \ln P_A}{\partial(1/T)} = \frac{-1}{\left(\frac{v_A}{v_B} - \frac{v'_A}{v'_B}\right) R} \left[\frac{\Delta H^0_{\text{subl}}}{v_B} - \frac{\Delta H^0_{\text{subl}}}{v'_B}\right]$$

(3.23)

A similar equation can be derived for the intercepts (entropy changes).

For the case of water vapor over a pair of acid hydrates having $n$ and $n'$ waters we
substitute \( H_2O = A \), acid = \( B \), \( \nu_B = \nu_B' = 1 \), \( \nu_A' = n' \) into equation (3.23)

\[
\frac{\partial \ln P_{H2O}}{\partial (1/T)} = \frac{\Delta H^0_{\text{subl}} - \Delta H^0_{\text{subl}}}{(n - n')R}
\]

(3.24)

Similarly, for acid vapor over the pair of hydrates we have

\[
\frac{\partial \ln P_{\text{Acid}}}{\partial (1/T)} = \frac{n\Delta H^0_{\text{subl}} - n'\Delta H^0_{\text{subl}}}{(n - n')R}
\]

(3.25)

### 3.6.3 The HNO\(_3\)/H\(_2\)O Binary System

For the HNO\(_3\)/H\(_2\)O binary system we use the \( H^0_f \) values given in the CRC Handbook [Lide, 1993] and the heats of mixing the pure liquids at 198 K given by Forsythe and Giauque [1942] as well as their heats of fusion and heat capacities. Note that care must be taken to consistently use \( H^0_f \) values from the same source within a given calculation, as enthalpies of formation are much greater than those of vaporization and hence small differences in \( H^0_f \)'s would lead to large errors in \( \Delta H^0 \)'s. These values are summarized in Table 3.7 at their standard states.

As mentioned, our temperature of interest is around 200 K. Vapor phase enthalpies are adjusted from 298 K to 200 K using linear fits to the heat capacity data given in the JANAF tables [Chase et al., 1985]. For the liquid solutions and crystalline hydrates we use linear fits to heat capacity data reported by Forsythe and Giauque [1942], as illustrated in Figure 3.26. For NAD we do not have temperature dependent heat capacity data below 270 K so there will be some uncertainty. Liquid phase \( C_p \) for NAD composition are extrapolated from Timmermans’ [1960] compilation of binary systems properties. As a rough estimate for crystalline NAD we
use a mean of NAM and NAT heat capacities over this temperature range.

Employing equation (3.19), we get \( H^{00}_f \) = -505.6 kJ/mole for NAM and -1108.1 kJ/mole for NAT (referenced to the elements at 298 K). Table 3.8 is produced in this manner, and Table 3.9 at a similar process for the entropies.

The slope of a \( \ln K_p \) vs. \( 1/T \) plot for NAT at 200 K is calculated to be, using equation (3.15), -27978, which agrees very well with previously reported values. Worsnop et al. [1993] measured -28520 ± 470, Smith [1990] fit -28100 ± 500 to Hanson and Mauersberger’s [1988a] measurements (and also calculated -27000 using a similar analysis to this one but without consideration of the heat capacities), and Mozurkewich [1993] calculated -27881 using an analysis which included heat capacity data. For the intercept, \( \Delta S^0/R \), we find a value of 74.0 (with pressures in atmospheres) whereas Worsnop et al. measured 78.7 ± 2.7, Smith obtained 76.5 ± 1, and Mozurkewich 75.3.

For nitric acid monohydrate we arrive at \( \ln K_p = 40.5 - 14495/T \), which may be compared to \( \ln K_p = (44.3 \pm 1) - (15330 \pm 500)/T \) from Smith’s analysis and \( \ln K_p = (44.1 \pm 1.7) - (15264 \pm 300)/T \) from Worsnop et al.’s observations. For the dihydrate we get \( \ln K_p = \Delta S^0 - 21102/T \) which can be compared to Worsnop et al.’s \( \ln K_p = (64.9 \pm 2.2) - (22630 \pm 360)/T \).

The slope of \( \log P_{H_2O} \) vs. \( 1/T \) at the NAT/NAM coexistence, that is, the right hand side of equation (3.24), is calculated to be 2927, which is in reasonable agreement with Hanson and Mauersberger’s [1988a] measured value of 2699. Similarly, we derive a value of 3368 for the slope of \( \log P_{HNO_3} \) vs. \( 1/T \), consistent with Hanson and Mauersberger’s [1988a] value of 3411. Other coexistence slopes are given in Table 3.10.
3.6.4 The HCl/H₂O Binary System

Thermodynamic data for the HCl/H₂O binary system are very limited. To the best of our knowledge, no heat capacity data have been reported for the liquid solutions and crystalline hydrates of this system. However, the estimated error due to the neglect of temperature of $H_i$'s might be small, as being the case with the HNO₃/H₂O binary system (less than 10 %).

The table entries are calculated in the same manner as for the nitric acid hydrates. The heat of vaporization of the trihydrate is estimated from the vapor pressure measurements of Hanson and Mauersberger [1990], and the hexahydrate heat of fusion is measured in this study.

Using equation (3.25) we calculate the slope of the log $P_{HNO₃}$ vs. $1/T$ over the ice/hexahydrate coexistence line to be 3526, which is consistent with our measured value of 3340. In Figure 3.27, the calculated HCl vapor pressures over the ice/hexahydrate coexistence mixture are compared with the measured values. The HCl vapor pressure at the ice/hexahydrate eutectic is obtained from the liquid vapor pressure data of Fritz and Fugnet [1956].

3.6.5 The H₂SO₄/H₂O Binary System

Here the individual values for the $K_p$'s are of less interest here because solid-vapor equilibria may not be maintained at the extremely low ambient mixing ratios of H₂SO₄, but the water vapor pressures over coexisting solids are of potential importance. H₂O vapor pressures over ice-hydrate coexistence systems are negligibly different from those of ice alone, in light of the fact that chemical potentials (or vapor pressures) should be equal when two phases are in
equilibrium. Using equation (3.24), we calculate a value of 2984 for the slope of \( \log P_{\text{HNO}_3} \) vs. \( 1/T \) over the tetra-dihydrate coexistence line, consistent with our measured value of 3236. We find excellent agreement between observed and predicted \( \text{H}_2\text{O} \) vapor pressures along the tetra-/dihydrate coexistence line (Figure 3.28).
TABLE 3.7. Components at standard state.

<table>
<thead>
<tr>
<th>Species</th>
<th>( H_{298} )</th>
<th>( S_{298} )</th>
<th>( H_{298} )</th>
<th>( \int C_p , dT )</th>
<th>( H_{200} )</th>
<th>( S_{298} )</th>
<th>( S_{200} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mole</td>
<td>J/mole/K</td>
<td>kJ/mole</td>
<td>kJ/mole</td>
<td>kJ/mole</td>
<td>J/mole/K</td>
<td>J/mole/K</td>
</tr>
<tr>
<td>liquid</td>
<td>liquid</td>
<td>gas</td>
<td>gas</td>
<td>gas</td>
<td>gas</td>
<td>gas</td>
<td>gas</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-285.830±.042</td>
<td>69.950±.79</td>
<td>-241.826±.42</td>
<td>-3.395</td>
<td>-245.221</td>
<td>188.834±.042</td>
<td>175.038</td>
</tr>
<tr>
<td>HCl</td>
<td>-167.15±.1</td>
<td>56.5±.2</td>
<td>-92.31±.1</td>
<td>-2.859</td>
<td>-95.169</td>
<td>186.902±.005</td>
<td>175.271</td>
</tr>
<tr>
<td>HNO(_3)</td>
<td>-174.18</td>
<td>155.679</td>
<td>-135.13</td>
<td>-4.687</td>
<td>-139.817</td>
<td>266.400</td>
<td>247.468</td>
</tr>
<tr>
<td>H(_2)SO(_4)</td>
<td>-813.989±.67</td>
<td>156.895±.08</td>
<td>-735.13±8.4</td>
<td>-7.383</td>
<td>-742.513</td>
<td>298.796±2.1</td>
<td>269.003</td>
</tr>
</tbody>
</table>

124
### TABLE 3.8. Enthalpies of the Binary Systems.

| Species      | $\Delta H_{298}^{mix}$ | $H^0_{298}$  | $T_{fus}$  | $\int C_p \,dT_{298}$ | $\Delta H_{fus}$ | $\int C_p \,dT_{fus}$ | $H_{200}$ | Slope of
<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>kJ/mole</td>
<td>kJ/mole</td>
<td>K</td>
<td>kJ/mole</td>
<td>kJ/mole</td>
<td>kJ/mole</td>
<td>kJ/mole</td>
<td>kJ/mole at 200K</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>-285.83$\pm$.042</td>
<td>273.15</td>
<td>-1.890</td>
<td>-6.0109</td>
<td>-2.420</td>
<td>-296.151</td>
<td>-50.929</td>
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<tr>
<td>HCl$\cdot$3H$_2$O</td>
<td>-16.974</td>
<td>-1041.614</td>
<td>248.4</td>
<td>-2689</td>
<td></td>
<td>-1038.03</td>
<td></td>
<td>-207.2</td>
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<tr>
<td>HCl$\cdot$6H$_2$O</td>
<td>-7.786</td>
<td>-1889.916</td>
<td>203.15</td>
<td>-5.472</td>
<td>-26.978</td>
<td>-1922.366</td>
<td>-355.87</td>
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<tr>
<td>NH$_3$•H$_2$O</td>
<td>-24.48</td>
<td>-473.569</td>
<td>235.48</td>
<td>-11.367</td>
<td>-17.514</td>
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<td>-505.446</td>
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<tr>
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<td>-1127.67</td>
<td>281.63</td>
<td>-3.521</td>
<td>-19.93$\pm$.48</td>
<td>-8.853</td>
<td>-1159.97</td>
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<td>233.67</td>
<td>-16.383</td>
<td>-18.08$\pm$.16</td>
<td>-5.991</td>
<td>-1469.82</td>
<td>-236.87</td>
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<td>-1723.36</td>
<td>236.76</td>
<td>-19.336</td>
<td>-23.37$\pm$.63</td>
<td>-5.792</td>
<td>-1771.86</td>
<td>-293.68</td>
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<td>-2014.47</td>
<td>244.88</td>
<td>-20.298</td>
<td>-29.73$\pm$.9</td>
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<td>-2070.12</td>
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<td>220.27</td>
<td>-43.072</td>
<td>-33.07$\pm$.11</td>
<td>-5.102</td>
<td>-2818.40</td>
<td>-481.95</td>
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125

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<th>Species</th>
<th>$S^0$ 298</th>
<th>$\int_{298}^{T_{fus}} \frac{C_p}{T} dT$</th>
<th>$\Delta S_{fus} = \frac{200}{T_{fus}} \int_{T_{fus}}^{200} \frac{C_p}{T} dT$</th>
<th>$S$ 206</th>
<th>Intercept of $R \ln K_p$ vs. $1/T$</th>
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<tr>
<td>liquid</td>
<td>liquid</td>
<td>$\Delta H_{fus}/T_{fus}$</td>
<td>crystal</td>
<td>crystal</td>
<td>at 200 K i.e., $\Delta S$</td>
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<tr>
<td>H$_2$O</td>
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<td>-6.6202</td>
<td>-22.006</td>
<td>-10.233</td>
<td>31.091</td>
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<tr>
<td>HCl•3H$_2$O</td>
<td>9.87</td>
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<td></td>
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<tr>
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<td></td>
<td>-132.8</td>
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<tr>
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<td>-84.6</td>
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<tr>
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<td>-114.3</td>
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<td>H$_2$SO$_4$•2H$_2$O</td>
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126
<table>
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<tr>
<th>Coexistence mixture</th>
<th>Calculated slope ( \log P_{\text{H}_2\text{O}} \text{vs.} 1/T )</th>
<th>Experimental slope: ( \log P_{\text{H}_2\text{O}} \text{vs.} 1/T )</th>
<th>Calculated slope of ( \log P_{\text{acid}} \text{vs.} 1/T )</th>
<th>Experiment slope: ( \log P_{\text{acid}} \text{vs.} 1/T )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ice: ( \text{HCl}\cdot 6\text{H}_2\text{O} )</td>
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<td>-3526</td>
<td>-3340</td>
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<td>-4145</td>
<td>-3968*</td>
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</tr>
<tr>
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<td>-7883</td>
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<td></td>
</tr>
<tr>
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<td>-3388</td>
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<tr>
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<td>-2819*</td>
<td>-3371</td>
<td>-3561*</td>
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<td>-2935</td>
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<td>-3320</td>
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</tr>
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<td>( \text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}:\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O} )</td>
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<td>-3236</td>
<td>-6310</td>
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</tr>
<tr>
<td>( \text{H}_2\text{SO}_4\cdot 6\frac{1}{2}\text{H}_2\text{O}:\text{H}_2\text{SO}_4\cdot 6\frac{1}{2}\text{H}_2\text{O} )</td>
<td>-2772</td>
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<td>-7155</td>
<td></td>
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</tbody>
</table>

* From Hanson and Mauersberger [1988a].
Figure 3.26 Heat capacity of the HNO₃/H₂O binary system.
Figure 3.27 Same as Figure 3.23 except for the dotted line, which is determined using equation (3.25) and the liquid HCl vapor pressure data of Fritz and Fuget [1956] at the ice/hexahydrate eutectic.
Figure 3.28 Same as Figure 3.14 except for the dotted line, which is determined using equation (3.24) and our measured liquid H\textsubscript{2}O vapor pressure at the di-/tetrahydrate eutectic.
Chapter 4

Physical Chemistry of Multi-Component Acid Systems of Stratospheric Importance

Vapor pressures of HNO₃ and HCl over H₂SO₄/HNO₃/H₂O and H₂SO₄/HCl/H₂O solutions as well as over H₂SO₄/HNO₃/HCl/H₂O solutions are measured in order to predict incorporation of stratospheric acids into background sulfate aerosols. From the data, Henry’s law solubility constants for these systems are determined and the equilibrium compositions of aqueous stratospheric aerosols are predicted as a function of ambient temperature and mixing ratios of H₂O and HNO₃. The results indicate that at the low temperatures characteristic of the stratosphere at high latitudes in the winter and spring, the HNO₃ content reaches levels of the order of 10 % wt in these sulfate aerosols. The results also reveal that the amount of dissolved HCl in the background sulfate aerosols is small when compared with dissolved HNO₃, but may be significant for the production of Cl₂ via the heterogenous reaction between ClONO₂ and HCl at low temperatures.

The identity of crystallized H₂SO₄/HNO₃/H₂O ternary solutions is examined from the
vapor pressure measurements, along with infrared spectroscopic and DSC measurements performed in our laboratory, showing that freezing of the supercooled H$_2$SO$_4$/HNO$_3$/H$_2$O solutions leads to the formation of a solid mixture consisting of nitric acid trihydrate (NAT) crystals and sulfuric acid tetrahydrate (SAT) crystals. A new mechanism for type I PSC formation is proposed and shown to reconcile many atmospheric observations.

4.1 Introduction

A current outstanding issue is whether the heterogenous reactions implicated in the PSC particles occur on background stratospheric aerosols as well. There have been several attempts to assess the role of background sulfate aerosols in promoting the release of active chlorine and affecting the NO$_x$ budget. Laboratory measurements [Mozurkewich and Calvert, 1988; Tolbert et al., 1988; Fried et al., 1991; Hanson and Ravishankara, 1991; Worsnop et al., 1991] have demonstrated that the heterogeneous reaction between N$_2$O$_5$ and H$_2$O proceeds readily on concentrated sulfuric acid solutions. Recent model calculations have also indicated that the same reaction may account for a significant fraction of the larger-than-expected ozone trend [Hofmann and Solomon, 1989; Brasseur et al., 1990; Rodriguez et al., 1991]. In particular, Hofmann and Solomon [1989] modeled the observed ozone depletions following the eruption of El Chichon and concluded that heterogenous reactions may have been responsible for part of the anomalously low ozone levels observed at mid- latitudes, albeit at lower rates.

To understand the role of the stratospheric background aerosols in chlorine activation, one issue of considerable scientific interest concerns compositions or solubilities of various
stratospheric acids in these aerosols. In particular, the amount of HCl in the supercooled aerosols is crucial in determining the direct reaction between ClONO₂ and HCl, which may be a dominant pathway for the heterogeneous formation of active chlorine during the early polar winter.

Recently, a number of authors have carried out laboratory investigations on the uptake of nitric acid by sulfuric acid solutions. Reihs et al. [1990] reported the vapor pressures of nitric acid in sulfuric acid solutions ranging from 58 to 87 weight percent over a temperature range from 188 to 240 K. Van Doren et al. [1991] examined uptake of nitric acid by aqueous sulfuric acid droplets at 283 K. Also, calculations of vapor pressures for the H₂SO₄/HNO₃/H₂O ternary system were reported by Jaecker-Voiron et al. [1990a, b], who parameterized the experimental vapor pressure data of Vandoni [1944].

The uptake of HCl in aqueous sulfuric acid droplets was studied by Watson et al. [1990] at 283 K. Also, the results obtained by Tolbert [1992] for a 60 % H₂SO₄ solution at 203 K indicate that stratospheric aerosol containing 60-75 % sulfuric acid has a very low equilibrium HCl concentration (less than 10⁻⁷ M).

Many of the previous studies hinge on measurements performed at room temperature and application of these results to the stratosphere requires long extrapolations to low temperatures. Furthermore, for the studies performed close to stratospheric conditions, the available information applies only to the vapor pressures of HNO₃ and HCl in rather concentrated sulfuric acid solutions (≥ 58 % wt). Hence, little is known about concentration and composition of background stratospheric aerosols at low temperatures.

The background stratospheric aerosols may also provide an essential link in the formation of PSCs. A commonly proposed view for the formation of PSCs involves the freezing of
background sulfate aerosols, with solid sulfuric acid hydrates providing condensation nuclei for the NAT or ice particles [Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990]. Other theories suggest that PSCs might consist of liquid or amorphous solid HNO₃ solutions [Hanson, 1990; Arnold, 1992], or nitric acid dihydrate (NAD) [Worsnop et al., 1993], although all these phases are thermodynamically less stable than NAT under polar stratospheric conditions. As will be discussed below, a significant amount of HNO₃ is incorporated into the background sulfate aerosols prior to the observed onset of type I PSCs; we propose that the mechanism for type I PSC formation is likely due to freezing of the ternary H₂SO₄/HNO₃/H₂O aerosols at low temperatures with crystallization of nitric acid trihydrate. The frozen particles then grow to form PSCs by condensation of additional amounts of HNO₃ and H₂O vapor.

4.2 Liquid H₂SO₄/HNO₃/H₂O and H₂SO₄/HCl/H₂O Ternary Systems

4.2.1 Experimental

Vapor pressures of the H₂SO₄/HNO₃/H₂O and H₂SO₄/HCl/H₂O systems were measured using a static technique, as described previously in section 3.2.1.

Bulk ternary solutions were prepared by diluting ~96.6 % H₂SO₄, ~70.7 % HNO₃, and ~37 % HCl with deionized water. These acids were analyzed before mixing by standard acid-based titration and density measurements. For small (≤ 1 % wt) nitric and hydrochloric acid content, 1 % HNO₃ and HCl solutions and 75 % H₂SO₄ were first prepared by diluting the concentrated acids. The 0.01, 0.1, and 1 % HNO₃ or HCl solutions in the ternary mixtures were
then prepared by successive dilutions of the 1 % HNO₃ or HCl and the 75 % H₂SO₄ with
deionized water. Typically, 4 cm³ liquid were used for the vapor pressure measurements.

4.2.2 Vapor Pressure Results

Vapor Pressures of H₂SO₄/HNO₃/H₂O Solutions

Vapor pressure measurements for the H₂SO₄/HNO₃/H₂O ternary system were performed
for samples with 20 different compositions, with H₂SO₄ ranging from 35 to 75 % wt and HNO₃
from 0.1 to 15% wt. Figures 4.1 to 4.3 show the HNO₃ and H₂O vapor pressures of selected
solutions. Coefficients of the least square fits in the form log P = A - B/T for all of the
investigated cases are summarized in Table 4.1 for HNO₃ and in Table 4.2 for H₂O. The results
show the expected variability of HNO₃ and H₂O vapor pressures as a function of acid
composition, namely increasing HNO₃ and decreasing H₂O vapor pressures with increasing
H₂SO₄ content (fixed HNO₃) and similarly with increasing HNO₃ content (fixed H₂SO₄). For a
given composition, the temperature dependency of the HNO₃ and H₂O vapor pressures in the
ternary system is well described by the Clausius-Clapeyron equation over the relatively narrow
temperature range investigated.

For most acid compositions the vapor pressure measurements were performed at least
twice; the results were reproducible typically within 5 %. We also examined the homogeneity
and the equilibrium condition of the system by changing the speed at which the solutions were
stirred: within experimental precision the results were insensitive to these changes. The estimated
Figure 4.1 (a) Nitric acid and (b) water vapor pressures over aqueous H₂SO₄/HNO₃/H₂O solutions for 35% wt sulfuric acid of various nitric acid contents. Weight percents of nitric acid are indicated in the figure. The solid lines are fits to the experimental data. The dashed-dotted lines are calculated HNO₃ vapor pressures according to Jaecker-Voirol et al. [1990a, b]. The dashed line represents H₂O vapor pressures for zero nitric acid, discussed in section 3.3.2.
Figure 4.2  
Same as Figure 4.1 except for 40 % wt sulfuric acid.
Figure 4.3  Same as Figure 4.1 except for 50% wt sulfuric acid.
TABLE 4.1. Coefficients $A$ and $B$ from a Least-Square Fit of

$\log P = A - B/T$ for HNO₃ Vapor Pressures in the HNO₃/H₂O/H₂SO₄ Ternary System

<table>
<thead>
<tr>
<th>wt % H₂SO₄</th>
<th>wt % HNO₃</th>
<th>$A$</th>
<th>$B$ (x 10³)</th>
</tr>
</thead>
<tbody>
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<td>35</td>
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<td>8.08</td>
<td>2.97</td>
</tr>
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<td>5.0</td>
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* $B$: Kelvin

$P$: torr
TABLE 4.2. Coefficients $A$ and $B$ from a Least-Square Fit of

\[ \log P = A - \frac{B}{T} \] for H$_2$O Vapor Pressures in the HNO$_3$/H$_2$O/H$_2$SO$_4$ Ternary System

<table>
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<tr>
<th>wt % H$_2$SO$_4$</th>
<th>wt % HNO$_3$</th>
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<th>$B \times 10^3$</th>
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<td>10.37</td>
<td>2.97</td>
</tr>
<tr>
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<td>0.1</td>
<td>11.21</td>
<td>3.21</td>
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</table>

* $B$: Kelvin

$P$: torr
error limit of the present data is about 10 %, considering temperature, background signal, and calibration uncertainties.

\textit{Vapor Pressures of H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O Solutions}

HCl and H\text{\textsubscript{2}}O vapor pressures were measured for solutions with nine different compositions, with H\text{\textsubscript{2}}SO\text{\textsubscript{4}} ranging from 35 to 60 % wt and HCl from 0.01 to 5 % wt. The HCl vapor pressure results for 0.1 % wt HCl solutions with a range of H\text{\textsubscript{2}}SO\text{\textsubscript{4}} content are shown in Figure 4.4.

As expected, the HCl vapor pressures over H\text{\textsubscript{2}}SO\text{\textsubscript{4}}/HCl/H\text{\textsubscript{2}}O solutions are substantially higher than the HNO\text{\textsubscript{3}} vapor pressures over H\text{\textsubscript{2}}SO\text{\textsubscript{4}}/HNO\text{\textsubscript{3}}/H\text{\textsubscript{2}}O solutions for a given acid composition and temperature. For the same 0.1 % wt HNO\text{\textsubscript{3}} and HCl in 50 % wt H\text{\textsubscript{2}}SO\text{\textsubscript{4}} solutions, for example, the HCl vapor pressure value is about a factor of 1000 higher than that of the HNO\text{\textsubscript{3}} level at 200 K. The dependence of HCl vapor pressure on temperature and acid composition is similar to that described above for HNO\text{\textsubscript{3}} in the H\text{\textsubscript{2}}SO\text{\textsubscript{4}}/HNO\text{\textsubscript{3}}/H\text{\textsubscript{2}}O solutions, i.e., increasing HCl vapor pressure with increasing H\text{\textsubscript{2}}SO\text{\textsubscript{4}} content (fixed HCl) and similarly with increasing HNO\text{\textsubscript{3}} content (fixed H\text{\textsubscript{2}}SO\text{\textsubscript{4}}).

We did not measure HCl vapor pressures in very concentrated sulfuric acid solutions ($\geq$ 70 % wt); the signals did not stabilize unless the solutions were vigorously stirred, indicating significant surface depletion of HCl and therefore a non-equilibrium condition. The effect of HCl surface depletion in a 60 wt % H\text{\textsubscript{2}}SO\text{\textsubscript{4}} and 0.1 wt % HCl solution is explicitly demonstrated in Figure 4.5, showing an initial rapid decline in the HCl signal followed by somewhat rather stable
Figure 4.4 HCl vapor pressures over aqueous H$_2$SO$_4$/HCl/H$_2$O solutions for 0.1 % wt HCl of various H$_2$SO$_4$ contents.
Figure 4.5 The HCl signal as a function of time over a 60 wt % H$_2$SO$_4$ and 0.1 wt % HCl solution at 210 K, demonstrating the effect of HCl surface depletion. The sample was initially stirred for 0.7 min, before sampling the vapors with the mass spectrometer.
readings upon opening the valve to the mass spectrometer. In this case, the sample was initially stirred in order to pump away the air in the sample cell until 2.3 min when beginning sampling by the mass spectrometer. The asymptotic readings in the HCl signal after 5 min probably suggest that a steady state is achieved between the HCl evaporation from the surface layer and the HCl diffusion in the underlying liquid. For dilute H$_2$SO$_4$ solutions ($\leq$ 35 wt %) the HCl surface depletion was not observed, even if the sample was stirred at a slow speed or was not stirred at all.

4.2.3 Henry’s Law Solubility Constants

$H_2SO_4/HNO_3/H_2O$ Solutions

A major consideration in describing mass transport and chemical kinetics of gas-liquid reactions is the equilibrium distribution of the reagent gas or gases between the two phases. For the case of $H_2SO_4/HNO_3/H_2O$ ternary solutions, the activity -and hence the vapor pressure- of nitric acid in aqueous sulfuric acid solutions depends on the extent of solvation of the HNO$_3$ molecule and on its subsequent liquid phase reactions:

$$HNO_3(g) \rightarrow HNO_3(aq) \quad (4.1)$$

$$HNO_3(aq) \rightarrow H^+ + NO_3^- \quad (4.2)$$

$$HNO_3(aq) + H^+ \rightarrow NO_2^+ + H_2O \quad (4.3)$$

The equilibrium process represented by reaction (4.1) can be expressed in terms of the Henry’s law constant, $H$ ($M \ atm^{-1}$), which relates gas and liquid phase concentrations for an ideal solution:
\[ [\text{HNO}_3(aq)] = P_{\text{HNO}_3} \, H \] (4.4)

Reactions (4.2) and (4.3) represent acid-base dissociation equilibria of the dissolved nitric acid. Deno et al. [1961] and Sampoli et al. [1985] concluded that at room temperature reaction (4.3) is only important for very high H$_2$SO$_4$ concentrations (> 85 % wt); this reaction therefore will not be considered here. In terms of reactions (4.1) and (4.2) these authors reported that at room temperature the extent of dissociation of HNO$_3$ is 96.4, 80.4, 22, and 0 % for H$_2$SO$_4$ concentrations of 20, 40, 60, and 80 % wt, respectively.

In considering the solubility of HNO$_3$ that undergoes rapid reversible aqueous-phase reaction (4.2) (acid-based ionization equilibria), an effective Henry’s law constant, $H^*$, can be defined in terms of the total amount of dissolved HNO$_3$ by including reactions (4.1) and (4.2) [Schwartz, 1986]:

\[ H^* = H\{1 + K_2[H^+]\} \] (4.5)

\[ [\text{HNO}_3 \text{ total}] = [\text{HNO}_3(aq)] + [NO_3^-] = P_{\text{HNO}_3} \, H^* \] (4.6)

where $K_2$ is the equilibrium constant for reaction (4.2). For HNO$_3$ in dilute H$_2$SO$_4$ solutions, the total amount of dissolved HNO$_3$ greatly exceeds that described by Henry's law (equation 4.4) alone so that $H^*$ greatly exceeds $H$.

In the absence of specific chemical forces, Henry’s law coefficients are well correlated with the physical properties of solute and solvent. However, for polar, protic solvents (such as water) chemical forces frequently dominate, and Henry’s law coefficients can differ greatly for similar solutes.

If the H$_2$SO$_4$ content is much higher than that of HNO$_3$ in the ternary system, contributions to $[H^+]$ in equation (4.5) are dominated by the dissociation of H$_2$SO$_4$. As a result,
for a given $\text{H}_2\text{SO}_4$ content the effective Henry’s law constant can be regarded as independent of the nitric acid concentration and, therefore, the $\text{HNO}_3$ pressure is linearly proportional to the concentration of total dissolved nitric acid. On the other hand, if the concentrations of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ are comparable, the effective Henry’s law constant for a given sulfuric acid content may depend on the $\text{HNO}_3$ content, and, as a result, the $\text{HNO}_3$ vapor pressure need not be linearly related to its total concentration. This behavior is illustrated in Figure 4.6, which plots the logarithm of the $\text{HNO}_3$ vapor pressure versus the logarithm of the $\text{HNO}_3$ molarity ($M_n$) at 220 and 195 K. Two regimes are readily apparent in the figures: for small $\text{HNO}_3$ concentrations, a nearly unit slope of the log $P$ versus log $M_n$ plot can be seen for the 40-75 % wt $\text{H}_2\text{SO}_4$ solutions, indicating a linear relationship between the $\text{HNO}_3$ vapor pressure and its concentration. The intercepts of the lines with the zero nitric acid axis are normally used to determine the Henry’s Law solubility constants. As the $\text{HNO}_3$ content increases, the linear relationship no longer holds. Complete dissociation of the $\text{HNO}_3$ molecule in the solution would result in a slope of 2 for the log $P$ versus log $M_n$ plot, if $[H^+]$ is formed predominantly from $\text{HNO}_3$, as is the case for solutions with relatively small $\text{H}_2\text{SO}_4$ concentrations. These considerations assume a value of unity for the $\text{HNO}_3$ activity coefficient. Slope values larger than 2 for the curves in Figure 4.6 for high $\text{HNO}_3$ contents indicate strong departures from ideality, i.e., increasing values of the activity coefficient. Thus, Henry’s law will not apply if the $\text{HNO}_3$ concentration is higher, because the intercepts determined at the zero $\text{HNO}_3$ limit will greatly differ from those determined at higher $\text{HNO}_3$ concentrations.

In the case of $\text{HNO}_3$, which physically dissolves in aqueous sulfuric acid solutions without irreversible reactions, the effective Henry’s law coefficient can be measured directly, by allowing
Figure 4.6 Nitric acid vapor pressure vs. nitric acid molarity for 35-75 % wt sulfuric acid solutions at 220 K.
the system to reach equilibrium and measuring \([HNO_3 \text{ total}]\) and \(P_{HNO_3}\), e.g., \(H^*\) can be derived from the vapor pressure data. Alternatively, \(H^*\) can be determined from time-dependent uptake experiments [see, for example, Reihs et al., 1990].

Effective Henry's law constants \(H^*\) in the limit of zero nitric acid concentration are determined from our vapor pressure data using equation (4.6). The temperature and concentration dependence of these constants is depicted in Figure 4.7. Table 4.3 lists the \(A\) and \(B\) coefficients from least square fits of the following form:

\[
\ln H^* = A + B/T
\]  
(4.7)

Note that the slopes of the lines in Figure 4.7 (which define the values of \(B\)) are the negative of the slopes for the lines corresponding to the most dilute HNO_3 solutions in Figures 4.1 to 4.3, as follows from the definition of \(H^*\) in equation (4.6). Alternatively, the temperature dependence of the Henry's law constant can be expressed by

\[
\ln H^* = -\Delta H/RT + \Delta S/R
\]  
(4.8)

where \(\Delta H\) and \(\Delta S\) are the enthalpy and entropy of condensation of HNO_3. Values of \(\Delta H\) and \(\Delta S\) are also listed in Table 4.3.

As can be seen in Figure 4.7, equation (4.7) is a reasonable approximation over the relatively small temperature range of our measurements. It follows from the Clausius-Clapeyron equation that \(B\) can be identified with an enthalpy change [Denbigh, 1981]:

\[
B = -\frac{\partial (\ln P_{HNO3})}{\partial (1/T)} = \frac{\partial (\ln H^*)}{\partial (1/T)} = \frac{H_g - H_i}{R}
\]  
(4.9)

where \(H_g\) is the molar enthalpy of HNO_3 in the gas phase and \(H_i\) is the partial molar enthalpy of HNO_3 \text{ total} in solution at the specific concentration and temperature applicable to \(P_{HNO3}\) and
Figure 4.7 Temperature dependence of the effective Henry's law constants for HNO₃ in 40-75 % wt sulfuric acid. The dashed-dotted lines are results for 58 % and 74 % sulfuric acid reported by Reihs et al. [1990]. The value at 283 K (△) is for 73% sulfuric acid from the work of Van Doren et al. [1991]. The two solid circles (•) are values for 60 and 75 % wt H₂SO₄ estimated from the data of Vandoni [1944].
TABLE 4.3. Effective Henry’s Law Constants $H^*$ for the H$_2$SO$_4$/HNO$_3$/H$_2$O Ternary System$^\dagger$:

Coefficients $A$ and $B$ for the Equation $\ln H^* = A + \frac{B}{T}$

<table>
<thead>
<tr>
<th>% H$_2$SO$_4$</th>
<th>$A$</th>
<th>$B \times 10^3$</th>
<th>$\Delta H$ kcal/mole</th>
<th>$\Delta S$ cal/mole/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>7.34x10$^{-7}$</td>
<td>7.22</td>
<td>-15.39</td>
<td>-32.22</td>
</tr>
<tr>
<td>50</td>
<td>4.87x10$^{-8}$</td>
<td>7.47</td>
<td>-14.84</td>
<td>-33.45</td>
</tr>
<tr>
<td>60</td>
<td>2.43x10$^{-8}$</td>
<td>7.30</td>
<td>-14.50</td>
<td>-34.82</td>
</tr>
<tr>
<td>70</td>
<td>6.31x10$^{-9}$</td>
<td>7.24</td>
<td>-14.38</td>
<td>-37.50</td>
</tr>
<tr>
<td>75</td>
<td>6.12x10$^{-9}$</td>
<td>7.03</td>
<td>-13.96</td>
<td>-37.56</td>
</tr>
</tbody>
</table>

$^\dagger$ $B$: Kelvin

$H^*$: $M$ atm$^{-1}$
$H^\prime$. $H_1$ (and hence $B$) varies with temperature in a complex way because of the multiple chemical equilibria involved, as given by equations (4.1) to (4.3); hence, equation (4.7) is not strictly valid. Some insight into the expected temperature dependency can be gained by estimating $B$ from equation (4.5):

$$B = \frac{\partial (\ln H^\prime)}{\partial (1/T)} = - \frac{1}{R} \left[ \Delta H_1 + \Delta H_2 \left( \frac{K_2}{K_2 + [H^+]_{\text{HNO}_3 \text{ total}}} \right) \right] = - \frac{1}{R} \left[ \Delta H_1 + \Delta H_2 \left( \frac{[\text{NO}_3^\cdot]}{[\text{HNO}_3 \text{ total}]} \right) \right]$$

(4.10)

where $\Delta H_1$ and $\Delta H_2$ are the enthalpy changes associated with reactions (4.1) and (4.2). The extent of dissociation of $\text{HNO}_3$ may change with temperature (reaction (4.2) is not thermoneutral), and hence $B$ may change with temperature as well. The partial derivative in equation (4.10) is obtained at constant $\text{HNO}_3 \text{ total}$, and for simplicity at constant $[H^+]$ as well, rather than at constant $\text{H}_2\text{SO}_4 \text{ total}$; also, concentrations, rather than activities, are used in equation (4.10). Nevertheless, the conclusion that $B$ varies with temperature remains valid, so that extrapolations over wide temperature ranges using equation (4.7) are likely to be inaccurate.

Also shown in Figure 4.7 are data on 58 % and 74 % wt $\text{H}_2\text{SO}_4$ solutions reported by Reihs et al. [1990] and on 73 % wt $\text{H}_2\text{SO}_4$ droplets by Van Doren et al. [1991] made at room temperature; both groups calculated the effective Henry's law constant on the basis of the time dependence of the measured nitric acid uptake efficiencies. Figure 4.7 also shows values at 273 K estimated from the data of Vandoni [1944].

The effective Henry's constants we obtained for a 60 % wt $\text{H}_2\text{SO}_4$ solution are in a good agreement with the values from Reihs et al. [1990] over a 58 % solution. However, the values we determined at low temperatures for a 75 % wt $\text{H}_2\text{SO}_4$ solution are significantly higher than the values reported by Reihs et al. [1990] for a 74 % wt $\text{H}_2\text{SO}_4$ solution, while our extrapolated
value at room temperature is less than that of Reihs et al. [1990] and Van Doren et al. [1991].
As indicated by Reihs et al. [1990], errors in estimating the diffusion coefficients of nitric acid
in sulfuric acid solutions may result in errors in the absolute value of $H^*$ determined indirectly
from their uptake studies. Their measurements yield the product of $H^*\sqrt{D}$, requiring an
estimation of the diffusion coefficient $D$. This was done by extrapolating room temperature
viscosity values (proportional to $1/D$) using the standard methods given by Perry [1963].
However, these extrapolations become unreliable at low temperatures, particularly as the glass
transition temperature is approached. For a 60 % H$_2$SO$_4$ solution this temperature is around 160
K [Vuillard, 1957]; the extrapolation yields a value of $10^3$ centipoise for the viscosity rather than
the expected value of about $10^{15}$ centipoise at that temperature. Furthermore, as noted by Reihs
et al. [1990], there is another limitation associated with the HNO$_3$ uptake experiment: this
method only permits determination of HNO$_3$ solubility in concentrated H$_2$SO$_4$ solutions (> 50
wt %). In dilute H$_2$SO$_4$ solutions the HNO$_3$ solubility is so high that the uptake virtually is time
independent.

A consideration of the slopes of the lines shown in Figure 4.7 provides further insight
into the above discrepancy. The slopes represent the difference between the enthalpy of HNO$_3$
in solution and that of gaseous HNO$_3$, as given by equation (4.9). Figure 4.8 shows the enthalpy
of condensation of HNO$_3$ as a function of H$_2$SO$_4$ wt %. Two points in this figure can be
estimated without measurements: in the 100 wt % H$_2$SO$_4$ solution all HNO$_3$ will be in the
molecular form (i.e., no dissociation) so that the enthalpy of HNO$_3$ condensation will be equal
to that of pure HNO$_3$ liquid (open circle), if one neglects reaction (4.3); in 0 wt % H$_2$SO$_4$
solution all HNO$_3$ will be fully dissociated and the enthalpy will be equal to the enthalpy of
Figure 4.8 Enthalpies of condensation of HNO₃ for the aqueous HNO₃/H₂SO₄/H₂O ternary system.
condensation of pure HNO₃ liquid added by the enthalpy of infinitive dilution (open triangle).

Enthalpies for the aqueous H₂SO₄/HNO₃/H₂O system relative to the pure liquids have been reported by McKinley and Brown [1942] at 273 K from calorimetry measurements; based on that work, we estimate values for the partial molar enthalpies of HNO₃ in solution between about -6.9 and -2.6 kcal/mole for 40 % to 75 % wt H₂SO₄ solutions. When added to the enthalpy of evaporation of pure HNO₃ (-9.4 kcal/mol) these values are in reasonable agreement with those obtained from the slopes corresponding to our vapor pressure measurements (Figure 4.8); as discussed above, we expect some change in these slopes with temperature, but such change is minor in this context (i.e., for a 50 % wt H₂SO₄ solution the slope for the water vapor pressure corresponds to -12.6 kcal/mol at 298 K [Zeleznik, 1991] and to -11.8 kcal/mol at 200 K given in section 3.3.2). The enthalpy change corresponding to the results of Reihs et al. [1990] for a 74 % wt H₂SO₄ solution is about -7.1 kcal/mol. This value is ~30 % smaller than the enthalpy of condensation of pure HNO₃, and would imply that mixing liquid HNO₃ with a 74 % wt H₂SO₄ solution is an endothermic process, clearly in disagreement with the observations of McKinley and Brown [1942]. As is seen in Figure 4.8, the enthalpy of HNO₃ condensation increases as H₂SO₄ content decreases, suggesting that there is an increasing dissociation of HNO₃ in this ternary system.

The theoretical work of Jaecker-Voirol et al. [1990a,b] provides equations for predicting partial pressures for the H₂SO₄/HNO₃/H₂O ternary system. In general, the values predicted by these equations are in poor agreement with our measured values (see Figures 4.1 to 4.3); the discrepancies range up to a factor of 3 for a 10 % HNO₃ and 35 % H₂SO₄ solution at 200 K. The main assumptions made by these authors are that equation (4.7) is valid over an extended
temperature range, and that the activity coefficients for the three components can be estimated using van Laar’s equations; in principle, though, these equations are applicable only to non-polar species in close to ideal solutions. Furthermore, calculations of the water vapor pressures for the liquid H₂SO₄/H₂O system show a difference of a factor of 12 using the two different methods suggested by Jaecker-Voirol et al. (one method for the zero nitric acid limit in the H₂SO₄/HNO₃/H₂O ternary system, and the other for the H₂SO₄/H₂O binary system). In addition, as discussed earlier, both sets of calculated water vapor pressures deviate significantly from our experimental results for the H₂SO₄/H₂O binary system.

In order to estimate equilibrium aerosol compositions under stratospheric conditions, it is instructive to express the measured HNO₃ vapor pressures as a function of the composition of the liquid at a given temperature:

\[
\log P_{\text{HNO}_3} = a_1 + a_2 y + \log x + a_3 x
\]  
(4.11)

and for H₂O vapor pressures:

\[
\log P_{\text{H}_2\text{O}} = b_1 + b_2 x + b_3 y + b_4 \log y + b_5 \log^2 y + b_6 \log^3 y
\]  
(4.12)

where \(x\) and \(y\) are weight fractions of nitric and sulfuric acids in the ternary solutions (i.e., \(x = 0.3\) for a 30 % wt solution). The first three terms in equation (4.11) represent ideal straight-line behavior in Figure 6: that is Henry’s law; the fourth term accounts for the non-linearity apparent in the figure at higher nitric acid concentrations. Our results indicate that the temperature dependency of each of the coefficients \(a_i\) (\(i = 1, 3\)) and \(b_j\) (\(j = 1, 6\)) can be represented within experimental error by an expression of the form of equation (4.7); the corresponding parameters are given in Tables 4.4 and 4.5. The vapor pressures estimated with these equations differ typically by 5 %, and at most by 20 % from our measured values. These empirical relations are
TABLE 4.4. Parameters to Be Used in Equation (4.11)\textsuperscript{\dagger} for Estimating HNO\textsubscript{3} Vapor Pressures in the HNO\textsubscript{3}/H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{2}O Ternary System

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(a_1)</td>
<td>8.10</td>
<td>-3.32</td>
</tr>
<tr>
<td>(a_2)</td>
<td>5.15</td>
<td>-0.50</td>
</tr>
<tr>
<td>(a_3)</td>
<td>3.21</td>
<td>-0.79</td>
</tr>
</tbody>
</table>

\(\log P_{\text{HNO}_3} = a_1 + a_2y + \log x + a_3x\)

\(a_i = A + B/T\) (i = 1, 3)

\(T:\) Kelvin

\(P_{\text{HNO}_3}:\) torr
TABLE 4.5. Parameters to Be Used in Equation (4.12) for Estimating H₂O Vapor Pressures in the HNO₃/H₂SO₄/H₂O Ternary System

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>B (x 10³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b₁</td>
<td>9.70</td>
<td>-2.22</td>
</tr>
<tr>
<td>b₂</td>
<td>3.19</td>
<td>-1.32</td>
</tr>
<tr>
<td>b₃</td>
<td>-0.46</td>
<td>-0.71</td>
</tr>
<tr>
<td>b₄</td>
<td>-11.34</td>
<td>2.60</td>
</tr>
</tbody>
</table>

+ log\(P_{\text{H}_2\text{O}}\) = \(b₁ + b₂x + b₃y + b₄xy\)

\(b_i = A + B/T\) (i = 1, 4)

\(T: \text{Kelvin}\)

\(P_{\text{H}_2\text{O}}: \text{torr}\)
valid only for the acid concentration ranges employed in our measurements, i.e., 0 to 15 % wt HNO₃ and 35 to 75 % wt H₂SO₄.

\( \text{H}_2\text{SO}_4/\text{HCl/H}_2\text{O Solutions} \)

As is the case with the \( \text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O} \) solutions, the HCl vapor pressures depend both on its physical solubility and on its extent of dissociation:

\[
\text{HCl}(g) \rightarrow \text{HCl}(aq) \quad (4.13)
\]

\[
\text{HCl}(aq) \rightarrow \text{H}^+ + \text{Cl}^- \quad (4.14)
\]

As before, an effective Henry's law constant \( H^* \) can be defined as

\[
[H\text{Cl total}] = [\text{HCl(aq)}] + [\text{Cl}] = P_{\text{HCl}} \ H^* \quad (4.15)
\]

\[
H^* = H(1 + K_{1d}[H^+]) \quad (4.16)
\]

where \( K_{1d} \) is the acid dissociation constant.

Effective Henry's law constants were determined from our vapor pressure data using equation (4.15). Figure 4.9 illustrates the temperature dependence of these constants for 35, 40, 50 and 60 % wt sulfuric acid solutions; the parameters describing the lines in this figure are given in Table 4.6, along with the corresponding enthalpies and entropies of condensation of HCl in the sulfuric acid solutions.

Figure 4.10 presents the enthalpy of condensation of HCl as a function of \( \text{H}_2\text{SO}_4 \) concentration, showing a decrease in enthalpy with increasing \( \text{H}_2\text{SO}_4 \) concentration over the 35-60 wt % content. The decreasing enthalpy is consistent with the decreasing HCl dissociation when the \( \text{H}_2\text{SO}_4 \) content increases. Values for the two extreme cases at 0 wt % \( \text{H}_2\text{SO}_4 \) (solid
Figure 4.9 Temperature dependence of the effective Henry’s law constants for HCl in 35-60 % wt sulfuric acid. The dotted line is based on our measurements for a 60 wt % H₂SO₄ solution without stirring, and the long dashed lines are from Hanson and Ravishankara [1993]. The value at 222 K (open triangle) is for a 60% sulfuric acid from the work of Williams and Golden [1993].
TABLE 4.6. Effective Henry’s Law Constants $H^*$ for the H$_2$SO$_4$/HCl/H$_2$O Ternary System$^+$:

Coefficients $A$ and $B$ for the Equation $\ln H^* = A + B/T$

<table>
<thead>
<tr>
<th>% H$_2$SO$_4$</th>
<th>$A$</th>
<th>$B$ (x 10$^3$)</th>
<th>$\Delta H$ (kcal/mole)</th>
<th>$\Delta S$ (cal/mole/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35</td>
<td>1.17x10$^{-5}$</td>
<td>6.10</td>
<td>-12.12</td>
<td>-22.54</td>
</tr>
<tr>
<td>40</td>
<td>6.49x10$^{-6}$</td>
<td>5.88</td>
<td>-11.68</td>
<td>-23.73</td>
</tr>
<tr>
<td>50</td>
<td>1.02x10$^{-6}$</td>
<td>5.53</td>
<td>-10.98</td>
<td>-27.41</td>
</tr>
<tr>
<td>60</td>
<td>4.20x10$^{-7}$</td>
<td>4.92</td>
<td>-9.77</td>
<td>-29.16</td>
</tr>
</tbody>
</table>

$^+$ $B$: Kelvin

$H^*$: M atm$^{-1}$
Figure 4.10 Enthalpies of condensation of HCl for the aqueous HCl/H$_2$SO$_4$/H$_2$O ternary system.
triangle) and 100 wt % H₂SO₄ (open triangle) are estimated from the enthalpy of condensation of pure HCl liquid and enthalpy of infinitive dilution, as discussed above for the case of HNO₃/H₂O system.

Recently, a number of investigations have been carried out to examine the HCl solubility in sulfuric acid solutions. Williams and Golden [1993] reported HCl uptakes by 50-60 H₂SO₄ solutions at temperatures between 220 and 230 K using the Kundsen cell technique. Hanson and Ravishankara [1993] investigated both HCl uptakes and vapor pressures in H₂SO₄ solutions using a fast-flow reactor. Also, theoretical predictions of HCl solubility in the H₂SO₄ solutions were made by Luo et al. [1993].

As being the case for the HNO₃ uptake experiments, there are two potential problems associated with the time dependent HCl uptake experiments: this method can only be applied to concentrated H₂SO₄ solutions; the HCl liquid-phase diffusion constant in H₂SO₄ solutions needs to be estimated. To obtain the HCl diffusion constant in H₂SO₄ solutions, the majority of the HCl uptake studies employed the simple parameterized relationship $D = CxT/\eta$. Although Williams and Golden [1993] have recently measured the viscosity for a 60 wt % H₂SO₄ solution, there still is a great uncertainty regarding how reliably such a semi-empirical relation can be applied for describing HCl diffusion in H₂SO₄ solutions at low temperatures. Alternatively, Luo et al. [1993] suggested a theoretical expression for the diffusion constant derived from a cubic cell model for self-diffusion in pure liquids [Houghton, 1964]. It is also unclear how directly this model is related to binary solutions. On the contrary, determination of the effective Henry’s law solubility constants from vapor pressure data is rather simple, involving only a straightforward application of equation (4.15).
As shown in Figure 4.9, for 50-60 wt % H₂SO₄ solutions the effective Henry’s law constants determined from this work are a factor of 5 to 10 less than those derived from the uptake experiments [Williams and Golden, 1993; Hanson and Ravishankara, 1993] and from the theoretical predictions [Luo et al., 1993]. The discrepancy is likely to be attributed to the assumptions made on obtaining the liquid-phase diffusion constant by those studies.

Hanson and Ravishankara [1993] have also measured HCl vapor pressure measurements in the H₂SO₄/HCl/H₂O solutions. For dilute H₂SO₄ solutions (≤ 45 wt %), their results are in reasonable agreement with the present data. For concentrated H₂SO₄ solutions, however, their measurements yield vapor pressures which are a factor of 4 to 5 lower than the present data. Those authors prepared the liquid H₂SO₄/HCl/H₂O films of approximately 20 μm thickness, and therefore stirring was not possible in their experiments. As demonstrated previously (Figure 4.5), substantially higher HCl vapor pressures in concentrated H₂SO₄ solutions may lead to a significant HCl depletion on the surface layer if solutions are not properly stirred and, therefore, result in low HCl vapor pressures over the solutions and larger $H^*$ values. In fact, as showed in Figure 4.9, for the 60 wt % H₂SO₄ solution we could have measured essentially the same $H^*$ as that reported by Hanson and Ravishankara [1993] if the sample in our experiments had not been stirred. For dilute H₂SO₄ solutions, however, the effect of HCl surface depletion is negligible, because of the lower HCl vapor pressure in the solutions.

Hanson and Ravishankara [1993] reported that surface HCl depletion was negligible in their experiments, based on observations that no time-dependent HCl signal was observed for a 45 wt % solution and that the observed HCl vapor pressures showed no dependence on the mass flow rate in their experiments. However, as shown in Figure 4.5, the initial HCl depletion from
the surface layer may be a rapid and transient phenomenon, which may not be easily observable. Indeed, to carry out vapor pressure measurements in their system, the total pressure in the flow tube needed to be reduced from atmospheric pressure to less than 1 Torr, a process during which the initial HCl depletion could already have taken place. Consequently, the HCl vapor pressure measured by Hanson and Ravishankara [1993] would correspond to a steady state that was governed by the HCl surface evaporation and HCl diffusion through the underlying liquid and, therefore, had much smaller values than the true HCl vapor pressures of the solution. Also, these authors reported a noticeable change in the acid content related to evaporation of water in a 45 wt % H$_2$SO$_4$ solution in their uptake experiments. Note that H$_2$O vapor pressures in a 45 wt % H$_2$SO$_4$ solution (Figure 3.9) are actually comparable with HCl vapor pressures in a 0.1 wt % HCl and 45 wt % H$_2$SO$_4$ solution (Figure 4.4).

4.2.4 Equilibrium Compositions in Supercooled Stratospheric Aerosols

Steele and Hamill [1981] and Steele et al. [1983] discussed the deliquescence process of stratospheric aerosols with decreasing temperature. These authors estimated the aerosol compositions based on the water vapor pressure data reported by Gmitro and Vermeulen [1964] for the H$_2$SO$_4$/H$_2$O binary system. In a similar manner, using the data obtained in this work the equilibrium composition of stratospheric aerosols can be estimated considering HNO$_3$ and HCl as well.

At mid-latitudes, where the ambient temperatures in the lower stratosphere are between
215 and 225 K, the sulfate aerosol particles are composed mainly of 60-80 % wt aqueous sulfuric acid (Figure 4.11); only trace amounts of HNO₃ and HCl are incorporated into the particles. For example, for a nominal 60 % wt H₂SO₄ droplet at 215 K, the $H^*$ values are found to be $1.1 \times 10^7 M \text{ atm}^{-1}$ and $3.5 \times 10^3 M \text{ atm}^{-1}$ for HNO₃ and HCl respectively; this results in an equilibrium mixture of 0.06 % HNO₃ and 2.2 $\times 10^{-6}$ % HCl for ambient mixing ratios of 10 ppbv HNO₃ and 2 ppbv HCl at 100 mb (i.e., at about 16 km altitude). These results are consistent with those suggested earlier by Reihs et al. [1990] and by Waston et al. [1990] Therefore, both HCl and HNO₃ solubilities of background stratospheric aerosols in mid-latitude are well described in terms of the Henry's law behavior.

Equations (4.11) and (4.12) can be used to determine the equilibrium stratospheric composition of liquid aerosol droplets for a given temperature and mixing ratios of H₂O and HNO₃. The effect of temperature on this composition is presented in Figures 4.11 and 4.12; as expected, the predicted concentrations of HNO₃ in the aerosols increase rapidly at the lower temperatures. The curves in these figures were calculated assuming an environmental water partial pressure of 5 ppmv at 16 km altitude; the two solid lines were determined for environmental HNO₃ partial pressures corresponding to 10 ppbv and 5 ppbv at the same altitude. Also shown in Figure 4.11 is a curve estimated from our measured water vapor pressure values of supercooled H₂SO₄/H₂O solutions, similar to the one reported previously by Steele et al. [1983] We have assumed that the stratospheric aerosols remain in the liquid phase above 195 K [Dye et al., 1992; Pueschel et al., 1992] and that Kelvin effect is negligible, as justified by Steele et al. [1983].

The deliquescence process for a ternary droplet is essentially the same as that for a binary
Figure 4.11 Equilibrium sulfuric acid composition of background stratospheric aerosols as a function of temperature and ambient mixing ratios of water and nitric acid at 100 mb (5 ppmv H$_2$O and 5 ppbv or 10 ppbv HNO$_3$, ~16 km altitude). The dashed-dotted curve is for the case of zero nitric acid, discussed in section 3.3.2. Also shown in this figure is the freezing envelop of sulfuric acid solutions. The top axis labels the H$_2$SO$_4$ mole fraction for the H$_2$SO$_4$/H$_2$O binary system.
Figure 4.12 Equilibrium nitric acid composition of background stratospheric aerosols as a function of temperature and ambient mixing ratios of water and nitric acid at 100 mb (5 ppmv H2O and 5 ppbv or 10 ppbv HNO3, ~16 km altitude). The top axis labels the HNO3 mole fraction in the HNO3/H2SO4/H2O ternary system.
droplet: for a liquid H₂SO₄/HNO₃/H₂O mixture, a decrease in temperature at constant composition would cause a lowering of both the HNO₃ and the H₂O vapor pressures; hence, equilibrium is re-established subsequently by a change in composition through condensation of HNO₃ and H₂O vapors onto the droplet. The H₂SO₄ vapor pressure is so small that equilibrium with respect to this species is not established on the time scale of interest.

The most striking feature of the results plotted in Figure 4.12 is the sharp increase in the amount of dissolved HNO₃ as the temperature decreases from 210 to 197 K. Within this narrow temperature range, the equilibrium HNO₃ concentration increases from less than 0.1 % to about 10 % wt. For 10 ppbv HNO₃ and 5 ppmv H₂O at 100 mb, for example, we predict that the aerosols would consist of 12 wt % HNO₃ and 38 wt % H₂SO₄ at 195 K. Note also that the uptake of HNO₃ results in a decrease in H₂SO₄ concentration in the condensed phase for a given ambient H₂O mixing ratio: for 0 ppbv HNO₃ and 5 ppmv H₂O at 100 mb the aerosols would consist of about 45 wt % H₂SO₄, as is seen in Figure 4.11.

The present results can be used to estimate the distribution of nitric acid between the gas phase and the condensed phase as follows:

$$\frac{[HNO_3(aerosol)]}{[HNO_3(g)]} = \frac{(M_n L)}{(P_{HNO_3}/RT)} = \frac{(M_n LRT)}{P_{HNO_3}} \quad (4.17)$$

where $[HNO_3(aerosol)]$ is the amount of HNO₃ in the condensed phase per unit volume of air, $M_n$ is the equilibrium nitric acid concentration in the liquid solution (as given in Figure 4.12), $L$ is the volume fraction of the condensed phase in air, and $T$ and $P_{HNO_3}$ are the temperature and HNO₃ partial pressure in the stratosphere. Values for the volume fraction $L$ of stratospheric particulate are $10^{-14}$ for the "background" stratospheric aerosol, and $5 \times 10^{-12}$ for the volcanic aerosol found in winter at high-latitudes after the eruption of Mt. Pinatubo. [Hofmann et al., 168]
1992] Using these values along with $M_n = 2M$ for the equilibrium nitric acid composition at 197 K (10% wt nitric acid in 38% wt H$_2$SO$_4$) and $P_{\text{HNO}_3} = 10^8$ torr (10 ppbv at 100 mb), the ratios given by equation (4.17) are about $10^{-4}$ and $10^1$ for the background and enhanced volcanic aerosol, respectively. The characteristic time required to reach equilibrium can be estimated from the relation [Schwartz, 1986]

$$t = \frac{(2M_nRtd)}{(3\gamma_cP)}$$

(4.18)

where $d$ is the particle diameter and $\gamma_c$ is the accommodation coefficient, which is close to unity. Using a mean value for the particle diameter of 0.5 $\mu$m, the characteristic time is about 300 s, suggesting that equilibrium between condensed and gaseous nitric acid will be closely maintained.

Finally, it should be pointed out that due to increasing HNO$_3$ concentration in the background stratospheric aerosols at low temperatures ($T < 205$ K) the linear relationship or the Henry’s law solubility behavior no longer applies for describing HNO$_3$ solubility under conditions pertinent to the polar stratosphere, in light of the arguments presented in section 4.2.3, i.e., that increasing HNO$_3$ in H$_2$SO$_4$ solutions causes departures of the H$_2$SO$_4$/HNO$_3$/H$_2$O ternary solutions from ideality. On the other hand, the equilibrium HCl concentration found in background aerosols would be small under stratospheric conditions (less than 0.1 wt % at temperatures below 195 K). As a result, Henry’s law will be valid for describing HCl solubility throughout the stratosphere. In addition, because at low temperatures the background sulfate aerosols will take up enough HNO$_3$ vapor and consequently lead to formation of the H$_2$SO$_4$/HNO$_3$/H$_2$O ternary system, it should be more appreciate to address the HCl solubility of stratospheric background aerosols in terms of the H$_2$SO$_4$/HNO$_3$/HCl/H$_2$O quaternary system, rather than in the H$_2$SO$_4$/HCl/H$_2$O ternary system. That is to be presented next.
4.3 Liquid $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}$ Quaternary System

4.3.1 HCl Vapor Pressures

HCl vapor pressure measurements in the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}$ quaternary system were carried out in the same manner as those for the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4/\text{HCl}/\text{H}_2\text{O}$ ternary systems. Compositions of the quaternary solutions were chosen to be close to those predicted for stratospheric aerosols at low temperatures as discussed above, with the $\text{H}_2\text{SO}_4$ content ranging from 25 to 40 wt % and $\text{HNO}_3$ from 5 to 20 wt %. For all the investigated cases the HCl concentration in the quaternary solutions was 0.1 wt %.

Results of HCl vapor pressures in the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}$ solutions are shown in Figure 4.13 and coefficients for the least squares fits in the form of $\log P_{\text{HCl}} = A - B/T$ are given in Table 4.7. As is the case with the ternary systems, over the relative narrow temperature range investigated HCl vapor pressures in the quaternary solutions still can be described by the Clausius-Clapeyron equation for a given composition. It is also seen in Figure 4.13 that the HCl vapor pressure increases as the $\text{H}_2\text{SO}_4$ content decreases, even if the total acid concentration remains constant for the four measured compositions (i.e., 45 wt %). The increasing HCl vapor pressure with increasing $\text{H}_2\text{SO}_4$ is likely due to the high affinity of $\text{H}_2\text{SO}_4$ to $\text{H}_2\text{O}$ molecules, which tends to decrease solvation and hence to drive away the other molecules in the solution.

It is also noticed that the presence of minor amounts of HCl does not noticeably change both the $\text{H}_2\text{O}$ and $\text{HNO}_3$ vapor pressures of the system within experimental uncertainty, suggesting that the discussions made above on equilibrium concentrations of $\text{HNO}_3$ and $\text{H}_2\text{SO}_4$ in stratospheric background aerosols are still valid even if HCl vapor is included.
4.3.2 HCl Henry’s Law Solubility Constant

As discussed previously, in the case of no chemical loss reactions in the liquid phase, effective Henry’s law coefficients can be derived directly from the vapor pressure data. Mass scans of the quaternary solutions at low temperatures did not exhibit any new mass peak over the entire mass spectra, indicating that this assumption still holds for the H₂SO₄/HNO₃/HCl/H₂O solutions. As a result, effective Henry’s law solubility constants for HCl in the quaternary system can be determined using equation (4.15).

Figure 4.14 shows the temperature dependence of these constants for the four investigated cases; the parameters describing the lines in the figure are given in Table 4.8. As before, for a given composition the HCl solubility in H₂SO₄/HNO₃/H₂O solutions increases with decreasing temperature in Figure 4.14. The HCl solubility also increases with decreasing H₂SO₄ content, even if the total acid concentration in the solutions is fixed.

4.3.3 Equilibrium HCl Concentration in Supercooled Stratospheric Aerosols at Low Temperatures

From the HCl solubility data discussed in sections 4.2.3 and 4.3.2, the equilibrium concentration of HCl in the stratospheric background aerosols can be estimated, using the same approach as that employed to derive the equilibrium concentration of HNO₃ in the background aerosols. As before, the Henry’s law solubility constants can be parameterized in the following
functional form:

$$\log H = a_1 + a_2 x + a_3 y + a_4 xy$$  \hspace{1cm} (4.19)$$

where $x$ and $y$ are weight fraction for HNO$_3$ and H$_2$SO$_4$ in the solutions. To a good approximation, the temperature dependence of the coefficients can be represented by an expression of the form of equation (4.7); the results are summarized in Table 4.9. The $H^*$'s estimated with equation (4.19) differ typically by less 10 % from the measured values. Such a parameterization is valid only for the concentration ranges employed in this study, i.e., for 25 to 60 wt % H$_2$SO$_4$ and 0 to 25 wt % HNO$_3$.

Subsequently, by specifying HNO$_3$ and H$_2$O partial pressures in the stratosphere, equilibrium concentrations of HNO$_3$ and H$_2$SO$_4$ in the background aerosols can be estimated from equation (4.11) and (4.12) as a function of temperature. These values, in turn, can be substituted into equation (4.19) to calculate the $H^*$'s, yielding the HCl solubility constant in the quaternary background aerosols.

Figure 4.15 presents the HCl solubility constant in the background aerosols as a function of stratospheric temperature. The solid curves correspond to the HCl solubility constants in the H$_2$SO$_4$/HNO$_3$/H$_2$O ternary system, whereas the dashed curves correspond to those predicted in the H$_2$SO$_4$/H$_2$O binary system (i.e., excluding the presence of HNO$_3$). The three sets of curves are determined for 10 ppbv HNO$_3$ and for 5, 3, and 2 ppmv H$_2$O at 100 mb (~16 km), respectively. As expected, the HCl solubility increases with decreasing temperature in both systems. At low temperatures, the $H^*$ values predicted for ternary aerosols exceed slightly those predicted for the binary aerosols. This is likely to be attributed to the fact that at low temperatures ($T < 200$ K) the H$_2$SO$_4$ content in the H$_2$SO$_4$/HNO$_3$/H$_2$O aerosols is smaller than
Figure 4.13 HCl vapor pressures over various HCl/HNO₃/H₂SO₄/H₂O quaternary solutions: (a) 25 wt % H₂SO₄ and 20 wt % HNO₃; (b) 30 wt % H₂SO₄ and 15 wt % HNO₃; (c) 35 wt % H₂SO₄ and 10 wt % HNO₃; (d) 40 wt % H₂SO₄ and 5 wt % HNO₃. For all the solutions the HCl concentration is 0.1 wt %.
TABLE 4.7. Coefficients $A$ and $B$ from a Least-Square Fit of

$log P = A - \frac{B}{T}$ for HCl Vapor Pressures in the H$_2$SO$_4$/HNO$_3$/HCl/H$_2$O Quanternary System

<table>
<thead>
<tr>
<th>wt % H$_2$SO$_4$</th>
<th>wt % HNO$_3$</th>
<th>wt % HCl</th>
<th>$A$</th>
<th>$B \times 10^3$</th>
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</thead>
<tbody>
<tr>
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<td>15</td>
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</tr>
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<td>0.1</td>
<td>6.92</td>
<td>2.63</td>
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<tr>
<td>40</td>
<td>5</td>
<td>0.1</td>
<td>6.86</td>
<td>2.63</td>
</tr>
</tbody>
</table>

* $B$: Kelvin

$P$: torr
Figure 4.14 Temperature dependence of the effective Henry's law constants of HCl in the HCl/HNO₃/H₂SO₄/H₂O quaternary solutions: (a) 25 wt % H₂SO₄ and 20 wt % HNO₃; (b) 30 wt % H₂SO₄ and 15 wt % HNO₃; (c) 35 wt % H₂SO₄ and 10 wt % HNO₃; (d) 40 wt % H₂SO₄ and 5 wt % HNO₃. For all the solutions the HCl concentration is 0.1 wt %.
TABLE 4.8. Effective Henry's Law Constants $H^*$ for the H$_2$SO$_4$/HNO$_3$/HCl/H$_2$O Quaternary System$^\dagger$: Coefficients $A$ and $B$ for the Equation $\ln H^* = A + B/T$

<table>
<thead>
<tr>
<th>wt % HNO$_3$</th>
<th>wt % H$_2$SO$_4$</th>
<th>$A$</th>
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</tr>
<tr>
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<td>40</td>
<td>-10.20</td>
<td>5.34</td>
</tr>
</tbody>
</table>

$^\dagger$ B: Kelvin

$H^*$: $M$ atm$^{-1}$
TABLE 4.9. Parameters to Be Used in Equation (4.19)† for Estimating HCl Solubility Constants in the HNO$_3$/HCl/H$_2$SO$_4$/H$_2$O Quaternary System

<table>
<thead>
<tr>
<th></th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$b_1$</td>
<td>70.752</td>
<td>-0.193</td>
</tr>
<tr>
<td>$b_2$</td>
<td>-0.159</td>
<td>-9.792x10$^{-4}$</td>
</tr>
<tr>
<td>$b_3$</td>
<td>-0.598</td>
<td>1.144x10$^{-3}$</td>
</tr>
<tr>
<td>$b_4$</td>
<td>-7.626x10$^{-3}$</td>
<td>5.822x10$^{-5}$</td>
</tr>
</tbody>
</table>

† log$H^*$ = $c_1 + c_2x + c_3y + c_4xy$

$c_i = A + B/T$ ($i = 1, 4$)

$T$: Kelvin

$H^*$: $M$ atm$^{-1}$
Figure 4.15 HCl solubility constant as a function of stratospheric temperature. The three sets of curves correspond to 10 ppbv HNO₃ and to 5, 3, and 2 ppmv H₂O at 100 mb, respectively. The solid curves represent HCl solubility in the HNO₃/H₂SO₄/H₂O ternary aerosols, whereas the dashed curves represent the HCl solubility in the H₂SO₄/H₂O binary aerosols.
that in the H$_2$SO$_4$/H$_2$O aerosols, as noted earlier. At higher temperatures, both the solid and
dashed curves converge, which is consistent with the small HNO$_3$ solubility and thus negligible
amount of HNO$_3$ in the sulfate aerosols at mid-latitudes.

Using the results displayed in Figure 4.15, the equilibrium concentration of HCl in the
background aerosols can be calculated from the $H^*$'s and the gas phase HCl concentration in the
stratosphere. For 2 ppbv HCl, 10 ppbv HNO$_3$, and 5 ppmv H$_2$O at 100 mb and at 197 K, for
example, $H^* = 10^7 \; M \; \text{atm}^{-1}$, leading to an HCl concentration of ~0.1 wt %. Such an HCl
concentration may be significant for the reaction between ClONO$_2$ and HCl occurring on the
supercooled background aerosols, as pointed out by Molina et al. [1993]. Therefore, in the
extremely cold parts of the stratosphere where the sulfate aerosols contains more H$_2$O and the
HCl solubility is corresponding higher, heterogeneous reactions such as the one between ClONO$_2$
and HCl could become important. At mid-latitudes, on the other hand, the extremely small
amount of HCl available in the background sulfate aerosols means that those reactions are likely
to be unimportant, which is consistent with model calculations, showing that most of the
discrepancy between the measured and calculated ozone concentrations at mid-latitudes can be
accounted for by including only the heterogeneous reaction between N$_2$O$_5$ and H$_2$O [Arnold et
al., 1991; Rodriguez et al., 1991].

4.4 Crystallized H$_2$SO$_4$/HNO$_3$/H$_2$O Ternary Solutions

Another current outstanding issue of heterogeneous chemistry in the polar stratosphere
concerns the mechanism of type I PSC formation. There have been several proposed scenarios
for nucleation and growth of type I PSCs, among which is the assumption that nucleation followed by co-condensation of HNO$_3$ and H$_2$O occurs on already frozen sulfuric acid aerosols to form NAT particles [Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990]. Alternatively, there has been some discussion of the possibility that the nitric acid containing particles are supercooled liquids [Hanson, 1990] composed of a ternary mixture of HNO$_3$/H$_2$SO$_4$/H$_2$O [Crutzen et al., 1988; Hofmann and Deshler, 1990]. Recently, Worsnop et al. [1993] suggested that nucleation and persistence of metastable HNO$_3$•2H$_2$O may be favored in PSCs over the slightly more stable HNO$_3$•3H$_2$O.

As mentioned in section 2.1, type I PSCs occur near saturation ratios of HNO$_3$ with respect to NAT of 1 in the Antarctic [Fahey et al., 1989], while saturation ratios with respect to NAT of 10 or greater are observed to be necessary for the main occurrence of type I PSCs in the Arctic [Dye et al., 1990; Dye et al., 1992]. The proposed free-energy barrier against nucleation [Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990] has difficulty to explain, for these two cases, the similarities in particle size distribution, but differences in the apparent saturation ratio at which PSCs occur. Also, as is shown in section 4.2.4, there is a rapidly, but yet gradually increasing amount of nitric acid which is incorporated into the background sulfate aerosols as the stratosphere is cooled. The possibility that type I PSCs consist of supercooled nitric acid aerosols [Hanson, 1990; Crutzen et al., 1988; Hofmann and Deshler, 1990] can be ruled out, because it is difficult to reconcile with the sudden increase in particle volume associated with PSC formation observed during the Airborne Arctic stratosphere Experiment (AASE) [Dye et al., 1990; Dye et al., 1992].

Prior to the onset of type I PSCs the amount of condensed nitric acid in stratospheric
sulfate aerosols is already quite high, approaching 10 % by weight. In this section laboratory experiments are presented on the formation and thermodynamics of frozen HNO$_3$/H$_2$SO$_4$/H$_2$O solutions, demonstrating that sulfuric acid tetrahydrate crystals and nitric acid trihydrate crystals are unambiguously identified when the solutions freeze.

4.4.1 Vapor Pressures

A small amount of liquid HNO$_3$/H$_2$SO$_4$/H$_2$O ternary solutions was placed at the bottom of the sampling vessel and slowly cooled to low temperatures. Occasionally, some samples crystallized spontaneously upon cooling to 190 K (samples with more HNO$_3$ tended to freeze more readily); if not, then the sample had to be cooled to ≤ 150 K and warmed to ~ 190 K, sometimes repeatedly, to induce crystallization. After the solid substrate was established and the signals stabilized the mass spectrometer data were recorded at mass 18 and 46.

As discussed in section 3.2.1., according to the Gibbs phase rule, when two crystalline hydrates are in equilibrium with the vapor in a ternary system there are two degrees of freedom, i.e., there are three components and three phases so $F = 2$. The two independent variables are temperature and pressure, suggesting that such an eutectic in a ternary system can exist over a range of vapor pressures at a given temperature.

In one set of experiments, vapor pressures were measured over frozen solutions containing 10 % wt HNO$_3$ and 50 % wt H$_2$SO$_4$ in the liquid phase. Initially, upon freezing, the substrate exhibited substantially high HNO$_3$, but very low H$_2$O vapor pressures. Subsequent addition of H$_2$O to the substrate resulted in lowering of the equilibrium HNO$_3$ vapor pressure, and vice
versa. Figure 4.16 shows the typical evolution of HNO$_3$ and H$_2$O signals before and after addition of gaseous HNO$_3$ to the substrate at 210 K. As shown in the figure, the change in the equilibrium H$_2$O pressure resulted from the change in the H$_2$O partial pressure clearly suggests that the composition of the substrate is altered.

Figure 4.17 summarizes equilibrium vapor pressures of HNO$_3$ and H$_2$O over the established solid mixture. In this case, the points representing the logarithm of the HNO$_3$ vapor pressure versus the logarithm of the H$_2$O vapor pressure lie consistently on the $n = 3$ lines for a given temperature, indicating the presence of NAT, as inferred from the Gibbs-Duhem equation. Also, the vapor pressure values agree well with those reported originally by Hanson and Mauersberger [1988a] for NAT. The vapor pressures of HNO$_3$ and H$_2$O initially attained when the substrate froze corresponded to those of the coexistence of HNO$_3$•H$_2$O and HNO$_3$•3H$_2$O. Addition of H$_2$O to the substrate converted HNO$_3$•H$_2$O to HNO$_3$•3H$_2$O and, then, changed its thermodynamic state until ice saturation was reached. In these isothermal experiments, a readjustment of the H$_2$O partial pressure in the sampling vessel is followed by a corresponding change in the HNO$_3$ vapor pressure on a time scale of less than a minute; the conversion of "H$_2$O-rich" to "HNO$_3$-rich" NAT requires only a minor change in the composition of the hydrate, occurring mostly in its surface layers [Molina, 1993].

At temperatures warmer than 200 K both the HNO$_3$ and H$_2$O vapor pressures exhibited discontinuities when approaching the coexistence of HNO$_3$•3H$_2$O and ice along an isotherm (line a-b in Figure 4.17), clearly indicating a phase transition. The H$_2$O vapor pressure at which the transition occurred was smaller than that of ice at that temperature, but followed closely the value of the liquid-solid phase boundary of sulfuric acid previously measured in section 3.3.2 (also see
Figure 4.16 Time evolution of mass spectrometer signals for $\text{H}_2\text{O} \ (m/e \ 18)$ and $\text{HNO}_3 \ (m/e \ 46)$ before and after addition of gaseous $\text{HNO}_3$ to a frozen solution consisting of 19 % wt $\text{HNO}_3$ and 50 % wt $\text{H}_2\text{SO}_4$ at 210 K.
Figure 4.17 Equilibrium vapor pressures of HNO₃ plotted against H₂O for a frozen solution containing 10 % wt HNO₃ and 50 % wt H₂SO₄ in the liquid phase. The dotted lines denote phase boundaries between ice, HNO₃•3H₂O, and HNO₃•H₂O as well as between the solid and liquid phases [Hanson and Mauersberger, 1988a]. The solid curve delineates the liquid-solid phase boundary of H₂SO₄•4H₂O, with the HNO₃ vapor pressure determined from the temperature and H₂O vapor pressure of H₂SO₄ freezing envelope and from the Gibbs-Duhem relation (Equation (3.3)).
Figure 4.18 Equilibrium H₂O vapor pressures from the data in Figure 4.17. The dotted-dashed lines represent phase boundaries between ice, H₂SO₄·6.5H₂O, H₂SO₄·4H₂O, and H₂SO₄·2H₂O as well as between the solid and liquid phases. The dotted line corresponds to H₂O vapor pressures of the coexistence of HNO₃·3H₂O and HNO₃·H₂O [Hanson and Mauersberger, 1988a].
Figure 4.19). The vapor pressure of HNO₃, on the other hand, coincided with the value of HNO₃·3H₂O at the temperature and H₂O vapor pressure defined by the sulfuric acid freezing envelop (line a-b in Figure 4.18). This implies that the solid mixture contains sulfuric acid tetrahydrate crystals.

Indeed, a phase transition -such as melting, or conversion to a different hydrate- usually requires a significant amount of one of the components to be condensed or evaporated, and hence, a larger response time, easily observable in our experiments. Such a situation arises when the H₂O partial pressure reaches the values represented by the line a-b in Figure 4.17: melting of SAT at constant temperature and Pₜₐₗ is accompanied by the condensation of H₂O vapor, because under those conditions the mole fraction of H₂O in the liquid in equilibrium with SAT is significantly larger than 4:1. This transition corresponds to a state of four-phase equilibria in the phase diagram: at this point, with one gas, one liquid, and two solids, there is only one degree of freedom at equilibrium according to equation (3.1), and, consequently, the vapor pressures are uniquely determined.

The vapor pressures of H₂O can be repeatedly regulated by addition of H₂O or HNO₃ to the solid solution. The bounds for the H₂O vapor pressures are as follows: the lower bound is the pressure over the coexistence of HNO₃·H₂O and HNO₃·3H₂O; the upper bound is the pressure over the coexistence of HNO₃·3H₂O and ice at below 200 K and over the sulfuric acid liquid-solid boundary at above 200 K (Figure 4.18). The highest values of the H₂O vapor pressures attained at warmer temperatures (between 220 and 200 K) are below the stability regime of H₂SO₄ higher hydrate (H₂SO₄·6.5H₂O). For example, at 210 K the value is 4.2×10⁻¹ Torr, about 25 % smaller than the ice vapor pressure at the same temperature, but is very close
to that of liquid-solid phase boundary of H$_2$SO$_4$•4H$_2$O, as presented previously in section 3.3.2. The eutectic of HNO$_3$•3H$_2$O and H$_2$SO$_4$•4H$_2$O was observed to persist above 220 K without melting.

Vapor pressures were also measured over a frozen solution of 12 % wt HNO$_3$ and 38 % wt H$_2$SO$_4$. Initially, H$_2$O vapor pressures similar to those of ice were observed at temperatures below 200 K, while the HNO$_3$ signals were near the level of background noises, probably indicating a solid solution consisting of the coexistence of ice and nitric acid trihydrate. As before, nitric acid trihydrate was readily identified by addition of HNO$_3$ to the substrate. During this process, however, care was exercised to avoid the possibility of nucleating HNO$_3$ hydrates with a large excess of HNO$_3$ vapor [Worsnop et al., 1993]. In one case, an attempt was made to evaporate the ice phase in the frozen solution of 12 wt % HNO$_3$ and 38 wt % H$_2$SO$_4$ by flowing dry helium over the sample. The temperature was kept constant at 195 K throughout the process. It was observed that, over the course of several hours, the H$_2$O vapor pressure dropped to values a factor of 5 to 10 lower than that of pure ice, while the HNO$_3$ vapor pressure rose noticeably, suggesting that the ice phase had evaporated on the surface layer. However, as soon as the helium flow was stopped, both the H$_2$O and HNO$_3$ signals quickly returned to their initial values. This is likely due to the inhomogeneity between the surface and interior of the solid sample during the experiment: as H$_2$O diffused from the underlying solid, both the H$_2$O and HNO$_3$ vapor pressures recovered. A similar phenomenon was also observed by Worsnop et al. [1993] for the HNO$_3$/H$_2$O binary system.

In some experiments, after complete solidification of the solution (~192 K), the sample was brought to warmer temperatures without addition of HNO$_3$. The evolution of HNO$_3$ and H$_2$O
vapor pressures with temperatures is depicted in Figure 4.19. A phase transition was observed at 200 K upon warming; above 200 K, the substrate appeared to turn into a liquid-like mixture. The temperature at which the phase transition occurred matched closely the eutectic point of ice and $\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}$ [Gable et al., 1950; Giauque et al., 1960]. The vapor pressures of $\text{H}_2\text{O}$ exhibited a discontinuity at this transition point, and then followed the curve corresponding to the liquid-solid phase boundary of $\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}$, until complete melting of the substrate at about 230 K. During this process, melting was observed to happen to $\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}$, but not to $\text{HNO}_3\cdot3\text{H}_2\text{O}$, since the $\text{HNO}_3$ vapor pressure still matched that of $\text{HNO}_3\cdot3\text{H}_2\text{O}$ for the temperature and $\text{H}_2\text{O}$ vapor pressure defined by the sulfuric acid freezing envelope. For experiments performed on various frozen solutions with 12-20 % wt $\text{HNO}_3$ and 30-40 % wt $\text{H}_2\text{SO}_4$ in the liquid phase, the data consistently showed the formation of $\text{HNO}_3\cdot3\text{H}_2\text{O}$, and $\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}$.

Experiments carried out with ternary solutions of various other initial compositions yielded similar results: the solids formed are ice, $\text{H}_2\text{SO}_4$ hydrates and/or $\text{HNO}_3$ mono- and trihydrate with vapor pressures equal to those of the hydrates formed separately in each of the two binary systems.

The formation of nitric acid trihydrate and sulfuric acid hydrates from freezing the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ ternary solutions is also supported by infrared spectroscopic and calorimetric observations performed in our laboratory [Molina et al., 1993]. Figure 4.20 presents infrared spectra of frozen ternary solutions of various compositions, showing the unique IR signatures which can be attributed to both HAT and $\text{H}_2\text{SO}_4$ hydrates. The characteristics of the infrared spectra is also summarized in Table 4.10. The formation of $\text{H}_2\text{SO}_4$ hydrates is also evident in
Figure 4.19 Temperature evolution of the equilibrium vapor pressures of HNO₃ and H₂O over a previously frozen solution containing 12 % wt HNO₃ and 38 % wt H₂SO₄ in the liquid phase, with symbols as in Figure 4.17.
Figure 4.20 Infrared spectra of various crystallized $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ solutions. The spectra of pure NAT, SAT, and SAH are shown in the figure for comparison. The numbers correspond to those given in Table 4.10.
Figure 4.21 DSC warming curves showing melting of crystallized H$_2$SO$_4$/HNO$_3$/H$_2$O samples. Also shown for comparison as the two upper traces are the warming curves of 20 and 50 wt % H$_2$SO$_4$ solutions. For the sample with 38.7 wt % H$_2$SO$_4$ and 9.3 wt % HNO$_3$ the solid-solid phase transition temperatures match closely those of the H$_2$SO$_4$/H$_2$O binary system: the peaks (a) near 200 K represent either the eutectic melting of ice/H$_2$SO$_4$ tetrahedrane (SAT) followed by crystallization into H$_2$SO$_4$ hemihexahydrate (SAH), or the solid-solid conversion of octahydrate into SAH; the coexistence mixture of ice/SAH has an eutectic near 211 K (peak b), which is little changed in the ternary eutectic; and the peritectic transformation of SAH to SAT occurs at 219 K (peak c), which is again essentially the same in the binary and ternary systems. The two small peaks (e and f) correspond to the melting of SAT at 230 K and NAT at 233 K, respectively. For the sample with 50 wt % H$_2$SO$_4$ and 10 wt % HNO$_3$ the peak (d) at 220 K most likely represents the eutectic melting of NAT and SAT, which is followed by the melting of SAT near 240 K (peak g).
Figure 4.22 Ternary diagram for the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ system. Superimposed upon this figure are the dilution curves (solid lines) for liquid stratospheric aerosols at 100 mb (~16 km) and at ambient mixing ratios of 5 ppmv $\text{H}_2\text{O}$; and 10 ppbv $\text{HNO}_3$ (a), 5 ppbv $\text{HNO}_3$ (b), and 2.5 ppbv $\text{HNO}_3$ (c). Also shown along the dilution lines are the equilibrium temperatures (dotted lines), the frost point of crystalline $\text{HNO}_3\cdot3\text{H}_2\text{O}$ (i.e., $S_{\text{NAT}} = 1$) (●), and the point at which the $\text{HNO}_3$ vapor pressure reaches a supersaturation of 10 with respect to NAT ($S_{\text{NAT}} = 10$) (■). The temperatures and compositions of the dilution curves are calculated from our $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ vapor pressure data and extrapolated below ~195 K to the intercepts on the $\text{HNO}_3/\text{H}_2\text{O}$ line estimated with the vapor pressure data of Hanson [1990]. For case (a) the $\text{HNO}_3/\text{H}_2\text{O}$ line is reached at 193.5 K; the ice frost point is 192.6 K for 5 ppmv $\text{H}_2\text{O}$ at 100 mb. The dashed curves are the eutectic lines reported by Carpenter and Lehrman [1925]; also indicated is the identity of the various solids that at equilibrium crystallize first upon cooling liquids with compositions bounded by the eutectic lines.
Table 4.10. Spectral characteristics of the crystallized $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ solutions along with the amounts that could separate into SAT, NAT, and ice by weight percent and information about spontaneous sample crystallization upon cooling to 190 K.

<table>
<thead>
<tr>
<th>Sample number</th>
<th>H$_2$SO$_4$ wt % in solution</th>
<th>HNO$_3$ wt %</th>
<th>SAT wt %</th>
<th>NAT wt %</th>
<th>Ice wt %</th>
<th>Crystallized</th>
<th>Dominant spectral signature</th>
<th>Other spectral features</th>
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<td>H$_2$SO$_4$$\cdot$4H$_2$O</td>
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<tr>
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<td>12.6</td>
<td>76.5</td>
<td>23.4</td>
<td>0</td>
<td>no</td>
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<tr>
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<td>52</td>
<td>47.9</td>
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<td>-</td>
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<tr>
<td>6</td>
<td>30</td>
<td>12.5</td>
<td>52</td>
<td>23.2</td>
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<td>35.3†</td>
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<td>40</td>
<td>6.6</td>
<td>69.4‡</td>
<td>12.3‡</td>
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<td>-</td>
</tr>
<tr>
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<td>22.3</td>
<td>24</td>
<td>38.7§</td>
<td>44.6§</td>
<td>16.7§</td>
<td>yes</td>
<td>H$_2$SO$_4$$\cdot$6.5H$_2$O</td>
<td>NAT</td>
</tr>
</tbody>
</table>

* Never crystallized.

† Or 52.1 wt % H$_2$SO$_4$$\cdot$6.5H$_2$O, 35.3 wt % NAT, 12.6 wt % ice.

‡ Or 87.8 wt % H$_2$SO$_4$$\cdot$6.5H$_2$O, 12.3 wt % NAT, 0 wt % ice.

§ Or 55.1 wt % H$_2$SO$_4$$\cdot$8H$_2$O, 44.6 wt % NAT, 0 wt % ice.
the DSC experiments (Figure 4.21): the calorimetric results are in very good agreement with the melting point determinations of Carpenter and Lehrman [1925], who concluded that there are no mixed hydrates for the entire range of possible compositions in the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ ternary system. Their eutectic lines bounding the stability regimes of different hydrates are shown as dashed lines in Figure 4.22, which shows the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ ternary phase diagram.

4.4.2 The Mechanism of PSC Formation

The nucleation and formation of $\text{HNO}_3\cdot3\text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}$ from freezing of the liquid $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ ternary solutions may play a crucial role in type I PSC formation. Indeed, the experimental conditions in our experiments closely resemble those in the polar stratosphere in terms of partial pressures and temperatures.

In the early winter period of the polar stratosphere the background aerosols are likely to consist of concentrated supercooled sulfuric acid droplets with only negligible $\text{HNO}_3$ [Steele and Hamill, 1981; Steele et al., 1983; Reihs et al., 1990]. As the stratosphere is cooled, condensation of nitric acid occurs, forming a supercooled ternary solution of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{H}_2\text{O}$ and leading to the formation of nitric acid containing particles. The expected compositions are shown as dotted lines in Figure 4.22 for three sets of stratospheric conditions, assuming constant $\text{H}_2\text{O}$ and $\text{HNO}_3$ mixing ratios for each line. During this process the environmental water and nitric acid are depleted by the amount of water and nitric acid absorbed in all particles. For the normal background aerosol, the growth of small $\text{HNO}_3$ aerosols can not deplete the supply of $\text{HNO}_3$ and large supersaturations of $\text{HNO}_3$ with respect to NA1 develop. ER-2 measurements
of NO$_3$ and cloud particles show a saturation ratio with respect to NAT of 10 or greater [Dye et al., 1990; Dye et al., 1992], prior to the onset of type I PSCs in the early Arctic winter. This would correspond to an equilibrium aerosol composition of 12 % wt HNO$_3$ and 38 % wt H$_2$SO$_4$, as estimated from the vapor pressure data of the liquid HNO$_3$/H$_2$SO$_4$/H$_2$O ternary system. As the stratosphere further cools (probably below 192 K), the background aerosols may freeze and, as being the case in our experiments, form sulfuric acid hydrate crystals and nitric acid trihydrate crystals. The observed sudden increase in particle volume accompanying PSC formation [Dye et al., 1990; Dye et al., 1992] must be attributed to the rapid condensation of HNO$_3$ on to the frozen background aerosols composed of HNO$_3$•3H$_2$O crystals, because of the already existing high supersaturation with respect to NAT in the air.

Although the atmospheric observations do not discriminate between a liquid-solid and a gas-solid nucleation mechanism, they are, however, compatible with our proposed mechanism, in light of the observed supercooling behavior for the ternary H$_2$SO$_4$/HNO$_3$/H$_2$O solutions [Beyer, 1993; Molina et al., 1993]: crystallization of those aerosols occurs readily for compositions and temperatures corresponding to $S_{\text{NAT}} \geq 10$. As shown in Figure 4.22, cooling from 196.5 to 193.5 K along line (a) changes the equilibrium HNO$_3$ concentrations from 10.4 wt % to about 49 wt % on the HNO$_3$/H$_2$O line ($S_{\text{NAT}}$ increases from 10 to 90). As a result, the equilibrium composition of the liquid droplets changes very rapidly as the ice frost point is approached. Hence, temperature fluctuations in the stratosphere are likely to induce crystallization, not because of the increase in the degree of supercooling for droplets of a given composition, but because of the change in the equilibrium composition: as the H$_2$SO$_4$ concentration decreases and the HNO$_3$ concentrations increases, the solutions crystallize more
readily [Molina et al., 1993].

We believe the above-proposed model is largely responsible for the observed type I PSC events in the early winter period of the Arctic and Antarctic.

The most commonly suggested PSC formation mechanism [Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990] assumes that frozen sulfate aerosols -consisting presumably of crystalline sulfuric acid hydrates- provide the nuclei for the condensation of NAT. Seeding experiments have shown that SAT crystals are not efficient nuclei for NAT crystallization in supercooled 3:1 H₂O/HNO₃ solutions [Beyer, 1993; Molina, 1993]. Hence, it appears unlikely for NAT crystals to condense on SAT crystals directly from the vapor phase. Similarly, other PSC formation mechanisms suggesting the condensation of liquid or amorphous solid H₂O/HNO₃ solutions as a first step [Hanson, 1990; Arnold, 1992] appear implausible: HNO₃ is much more likely to condense on preexisting liquid particles, a process which does not require nucleation. Furthermore, amorphous solid solutions are unstable at stratospheric temperatures: they can only be generated in the laboratory at much lower temperatures, and they crystallize or melt spontaneously upon warming. In addition, these phases are metastable with respect to NAT: in the stratosphere they would evaporate at temperatures several degrees below the NAT saturation point.

Worsnop et al. [1993] have recently proposed that type I PSCs consist of NAD, rather than NAT. Their conclusions are based on laboratory studies of deposition of HNO₃ and H₂O vapors on a glass surface: NAD nucleates readily in the NAD stability regime and persists even under conditions where it is metastable with respect to NAT. We did not observe NAD formation in our experiments involving nucleation from the liquid phase; furthermore, infrared
spectroscopic data show that NAD surfaces converts to NAT surfaces upon exposure to stratospheric water partial pressures [Middlebrook et al., 1992].

Finally, our proposed model does not include the previously suggested energy barrier for nucleating NAT on solid background aerosols [Poole and McCormick, 1987; Hamill et al., 1988; Wofsy et al., 1990] and, therefore, may explain the observed high concentrations of type 1 PSC particles [Dye et al., 1990; Dye et al., 1992; Pueschel et al., 1992], noted in section 2.1.
Chapter 5

Heterogeneous Interactions of ClONO$_2$ and HCl with Surfaces of Proposed Stratospheric Materials

The reaction probabilities for ClONO$_2$ + H$_2$O $\rightarrow$ HOCl + HNO$_3$ (1) and ClONO$_2$ + HCl
$\rightarrow$ Cl$_2$ + HNO$_3$ (2) have been investigated on sulfuric acid tetrahydrate (SAT, H$_2$SO$_4$$\cdot$4H$_2$O) surfaces at temperatures between 190 and 230 K and at reactant concentrations that are typical of the lower stratosphere, using a newly constructed fast-flow reactor coupled to a quadrupole mass spectrometer. The results indicate that the reaction probabilities as well as HCl uptake depend strongly on the thermodynamic state of SAT surface: they decrease significantly with decreasing H$_2$O partial pressure at a given temperature, and decrease with increasing temperature at a given H$_2$O partial pressure, as the SAT changes from the H$_2$O-rich form to the H$_2$SO$_4$-rich form. For H$_2$O-rich SAT at 195 K $\gamma_1 \approx 0.01$ and $\gamma_2 \geq 0.1$, whereas the values for H$_2$SO$_4$-rich SAT decrease by more than two orders of magnitude. At low concentrations of HCl, close to
those found in the stratosphere, the amount of HCl taken up by H$_2$O-rich SAT films corresponds to a coverage of the order of a tenth of a monolayer ($\approx 1 \times 10^{14}$ molecules/cm$^2$); H$_2$SO$_4$-rich SAT films take up 2 orders of magnitude less HCl ($< 10^{12}$ molecules/cm$^2$). Substantial HCl uptake at high HCl concentrations is also observed, as a result of surface melting. The data reveal that frozen stratospheric sulfate aerosols may play an important role in chlorine activation in the winter polar stratosphere via processes similar to those occurring on the surfaces of PSC particles.

Laboratory experiments are also presented to investigate the surface chemistry and mechanism of the heterogeneous reactions. The data provide evidence for the formation of a quasi-liquid layer on the PSC particles, which facilitate these heterogeneous reactions through solvation of the acid species.

5.1 INTRODUCTION

As discussed in the introduction, the heterogeneous reactions of primary interest in the stratosphere are as follows:

\[
\text{ClONO}_2 + \text{H}_2\text{O} \rightarrow \text{HOCI} + \text{HNO}_3 \quad (5.1)
\]

\[
\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3 \quad (5.2)
\]

\[
\text{HOCI} + \text{HCl} \rightarrow \text{Cl}_2 + \text{H}_2\text{O} \quad (5.3)
\]

\[
\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3 \quad (5.4)
\]

\[
\text{N}_2\text{O}_5 + \text{HCl} \rightarrow \text{ClNO}_2 + \text{HNO}_3 \quad (5.5)
\]

The important consequence of these reactions is that the relatively inert chlorine reservoir
molecules (ClONO$_2$, HCl) are converted into forms (Cl$_2$, ClNO$_2$) that release chlorine radicals readily upon photolysis. The concomitant suppression of gas-phase reactive nitrogen radicals (NO$_x$) is also crucial to the efficiency of ozone destruction since they react with halogen radicals to form relatively stable reservoir species, halting ozone depletion.

Also as discussed previously, the stratospheric particles which act as catalysts for these reactions are either background sulfate aerosols or polar stratospheric cloud particles. Two distinct types of polar stratospheric clouds (PSCs) have been proposed: type I is usually assumed to consist of nitric acid trihydrate, and type II to consist of water-ice [Toon et al., 1986; Crutzen and Arnold, 1986; Poole and McCormick, 1987; Hamill et al., 1988]; background stratospheric aerosols at mid-latitudes are liquid and composed mainly of 60-80% wt aqueous H$_2$SO$_4$ [Steele et al., 1983]. As suggested by this study and by recent field observations [Toon et al., 1993], at low temperatures ($T < 200$ K) such as those prevailing in the early polar winter stratospheric aerosols are composed of supercooled HNO$_3$/H$_2$SO$_4$/H$_2$O ternary solutions. Also, our laboratory work reveals that crystalline sulfuric acid hydrates may form and persist under temperature and water partial pressure conditions typical of the high-latitude stratosphere.

There have been several laboratory kinetic studies of reactions (5.1) to (5.4) on various proposed stratospheric materials: the reaction probabilities ($\gamma$'s) have been measured on water ice [Molina et al., 1987; Tolbert et al., 1987; Tolbert et al., 1988; Leu, 1988a,b] on NAT, [Quinlan et al., 1990; Moore et al., 1990; Hanson and Ravishankara, 1991; Leu et al., 1991; Hanson and Ravishankara, 1992; Abbatt and Molina, 1992], and on liquid sulfuric acid solutions [Hanson and Ravishankara, 1991; Golden et al., 1993]. In particular, reactions (5.1) and (5.2) have been shown to occur readily at stratospheric concentrations of ClONO$_2$ and HCl on surfaces
of water ice and NAT in coexistence with ice [Hanson and Ravishankara, 1991; Hanson and Ravishankara, 1992], and to vary strongly as a function of the thermodynamic state of the NAT surfaces [Abbatt and Molina, 1992]. Heterogeneous reactions occurring on frozen sulfuric acid surfaces were, however, previously thought to be of little importance in the stratosphere [Hanson and Ravishankara, 1991].

In this section we report measurements of the reaction probabilities of (5.1) and (5.2) on SAT surfaces, conducted at reactant concentrations characteristic of the stratosphere, that is, on the order of $10^9$ to $10^{10}$ molecule cm$^{-3}$ for ClONO$_2$ and HCl. Our results indicate that the reaction probabilities as well as HCl uptake depend strongly on the thermodynamic state of the SAT surface, which is determined by the temperature and H$_2$O partial pressure in equilibrium with the solid. The H$_2$O-rich forms are shown to be more reactive than the H$_2$SO$_4$-rich forms. At high HCl partial pressures substantial HCl uptake is observed, most likely as a result of substrate melting. The data reveal that frozen stratospheric sulfate aerosols play an important role in chlorine activation in the winter polar stratosphere via processes similar to those occurring on PSC surfaces.

We also investigate surface chemistry and mechanism of the heterogeneous reactions. We have recently proposed that in the present of HCl vapor a liquid-like layer forms on the surface of the solid particles in which HCl solvation occurs. We present laboratory studies to investigate this particular mechanism, showing that such a liquid-like layer indeed forms on surfaces of all proposed PSC materials under stratospheric conditions (i.e., water-ice, NAT, and SAT). The results confirm the ionic-type mechanism for reaction (5.1), which occurs essentially with no activation energy.
5.2 EXPERIMENTAL

5.2.1 The Molecular Beam Mass Spectrometer (MBMS) System

The experiments were performed in a newly constructed apparatus shown schematically in Figure 5.1, which consists of a tubular fast-flow reactor coupled to a differentially pumped, molecular beam sampling quadrupole mass spectrometer (Extrel EXM-400) for species detection.

The molecular beam mass spectrometer are composed an ionizer, a mass filter, and an ion detector. Gases entering the mass spectrometer are first ionized by electron bombardment to form positive ions, which are then focused into the quadrupole region by electrostatic lens. Ions having a selected mass-to-charge ratio pass through the filtering region and impinge on an ion detector to produce a signal. The mass spectrometer can filter both positive and negative particles: it is only positive ions that are produced, filtered, and detected in this study. Positive ion production is accomplished employing the most commonly used electron impact ionization. The average electron energy used in this work was 70 ev. Two types of ion detectors are available in the mass spectrometer system: a Faraday cup and an electron multiplier. The Faraday cup signal yields a direct measure of the ion density exiting the mass filter, and therefore, is useful for calibrations and diagnostic tests. Higher detection sensitivity can be obtained by the electron multiplier.

The operating pressure for the mass spectrometer was typically near $10^{-6}$ torr, whereas the pressure in the flow tube is in the range of 0.5 to 2 Torr. As shown in Figure 5.1, the flow tube was coupled to the mass spectrometer by a two stage differentially pumped vacuum system. The first stage vacuum chamber was evacuated by a 10" diffusion pump (Edwards Model CR
Figure 5.1 Schematic diagram of the experimental apparatus used to study the heterogeneous reactions on proposed PSC materials.
The second stage vacuum (mass spectrometer) chamber is evacuated by a turbomolecular pump (Seiko-Seiki Model STP-400, 400 L s\(^{-1}\)). The remain gas flow was pumped by a roughing pump (Edwards model E2M80, 27 L s\(^{-1}\) pumping speed); only a small fraction of the total gas of the main gas flow was sampled.

In this configuration, a small fraction of the main gas flow passed through a 1.0 mm diameter pin-hole into the first stage chamber evacuated by the 10" diffusion pump. The gas diffusing through this pin-hole was collimated by a 1.0 mm diameter skimmer cone (Beam Dynamics) mounted on the front of the vacuum chamber which housed the mass spectrometer. The two pin-holes were separated by a distance of about 0.7 cm. The resulting molecular beam was modulated at 200 Hz by a tuning fork chopper before entering an electron impact ionization region to produce positive ions. The mass filtered ions were collected at a conversion dynode and further amplified by a Channeltron Electron Multiplier, an Extrel Electrometer, and, when phase sensitive detection is employed, a lock-in amplifier (EG&G PAR Model 5209).

The pin-hole sizes were determined such that large enough gas was allowed to the ionizer of the mass spectrometer from the flow tube while not exceeding its operating pressure limit and the pumping speeds of the diffusion turbomolecular pumps. In Figure 5.2, the He flux out the 1.0 mm diameter pin-hole is plotted as a function of density in the diffusion pump. The slope of the line yields the effective pumping speed of the diffusion pump (10\(^4\) L s\(^{-1}\)). With 1 Torr total pressure in the flow reactor the pressures in the diffusion pumped chamber and the mass spectrometer chamber are 5x10\(^{-5}\) and 3x10\(^{-6}\) Torr, respectively. Under these operating conditions the pressure in the ionizer (the molecular beam pressure) is about 4 times greater than the chamber pressure, as determined by a separate set of experiments.
Figure 5.2 Flux of molecules through the 1 mm diameter pin-hole as a function of gas density in the first stage chamber evacuated by the 10" diffusion pump. Slope of the line is an empirical determination of the pumping speed of the diffusion pump and is $10^4$ L/s.
Figure 5.3 Sensitivity test of the MBMS system using SF$_6$ as an inert tracer species. The total pressures in the flow tube are labeled in this figure.
The sensitivity of this system was tested using SF$_6$ as an inert tracer species: with one Torr total pressure of helium in the flow tube the partial pressure of SF$_6$ detected with a S/N ratio of 2 is about 1x10$^{-8}$ Torr. Figure 5.3 shows examples of the SF$_6$ signals as a function of its density for three different total pressures in the flow tube.

5.2.2 The Flow Tube

The flow tube can be isolated from the mass spectrometer system by rotating a small O-ring seal valve with a spring loaded closure mechanism to cover the pin-hole. This design facilitated the coupling of the flow tube to the mass spectrometer with minimal spacing, and provided a convenient way for removing the flow tube for treatments, such as coating its inside wall with liquid H$_2$SO$_4$ solutions.

Two different 50-cm length flow tubes were employed in the experiments: the inner diameters are 2.2 and 2.8 cm, respectively. Both flow tubes are surrounded by inner jackets in which refrigerated ethanol is circulated. The outer jackets of the flow tubes are evacuated to provide thermal insulation. Three movable injectors are located at the upstream end of the flow tube: a jacketed injector (1.0 cm o.d.) kept warm by flowing a room temperature solution of ethylene glycol in water to add water vapor to the system, a center-located injector (0.3 cm o.d.) to introduce the reactant, and an injector (0.3 cm o.d.) to introduce other trace gas species such as HCl. The ethanol reservoir used to cool the flow tube was temperature-regulated by a combination of resistance heating and liquid nitrogen cooling. The coolant temperature was monitored with thermocouples located at the entrance and exit of the cooling jacket. The
temperature of the refrigeration system could be maintained or regulated between 190 and 230 K; the stability of the system was about \( \pm 0.5^\circ C \). Typically, the temperature variation over the length of the flow tube was less than 1 K.

For all experiments reported here the flow tube was operated at pressures between 0.5 and 2.0 Torr, and the average buffer gas (helium) velocities range from 1100 to 2000 cm s\(^{-1}\). Gas flows are monitored by electronic mass flow meters (Tylan Model FM-360), and the total flow tube pressure is monitored by a 10 Torr full scale pressure transducer (MKS Model 220CA) with an accuracy of \( \pm 0.5 \) mTorr.

Ice films were deposited on the cold walls of the flow tube by bubbling a known amount of He through a \( H_2O \) reservoir at room temperature. For all the experiments the thickness of ice films were estimated to be approximately 15 to 25 \( \mu m \).

To prepare a NAT film, an ice film was initially deposited. The film was then exposed to \( HNO_3 \) in the gas phase at partial pressures of \( (5 - 10) \times 10^{-5} \) Torr. Initially, the \( HNO_3 \) was taken up by the ice film, but, after a period of 30 to 60 min, the film became saturated with \( HNO_3 \) and the \( H_2O \) vapor pressure simultaneously dropped to values a factor of 5 to 10 lower than that of pure ice. By addition of small amounts of \( H_2O \) to establish the \( H_2O \) partial pressure in the flow tube the composition of the surface layers can be altered. Alternatively, NAT film can be produced by exposing an ice film to \( ClONO_2 \) at its partial pressures of \( (5 - 10) \times 10^{-6} \) Torr [Hanson and Ravishankara, 1992].

SAT surfaces were prepared by completely covering the inside wall of the flow tube with a liquid film of \( \sim57.7 \) wt \% \( H_2SO_4 \) solution and by quickly cooling the film to low temperatures. To ensure uniform wetting, the flow tube was first cleaned with a dilute HF solution or with a
chromic-sulfuric acid solution, and then rinsed with distilled water. Crystallization of the liquid coating normally occurred at about 200 K upon cooling, and the SAT surfaces were verified to melt within a degree of the pure SAT melting point [Gable et al., 1950]. Generally, upon freezing, the solid exhibited H$_2$O vapor pressures very close to those of pure ice, characteristic of the coexistence mixture of ice/tetrahydrate. By slowly raising the temperature and by flowing dry helium over the samples, a sudden drop in the water vapor pressure was observed after some time, suggesting that the ice phase had evaporated, leaving only SAT behind. The H$_2$SO$_4$-rich and H$_2$O-rich forms of the tetrahydrate could then be generated by controlling the equilibrium H$_2$O vapor pressure through addition or evaporation of small amounts of water at a constant temperature or by controlling the temperature at a constant H$_2$O partial pressure.

5.2.3 Reactant and Gas Sources

ClONO$_2$ was synthesized by the reaction between CIF and HNO$_3$, according to the procedure described by Schack [1967]. The purity of ClONO$_2$ samples was checked both by ultraviolet spectrophotometry at several wavelengths and by mass spectrometry, and was found to be greater than 90 % in the gas-phase, with Cl$_2$ being the major impurity. To deliver ClONO$_2$ to the flow tube, 0.5 to 10 sccm of helium passed through a ClONO$_2$ bubbler maintained at 195 K in a dry ice-acetone bath.

HOCl was prepared in the dark by mixing 75 ml of a NaOCl solution (6% active chlorine, Aldrich Chemical Co.) with 40 g of MgSO$_4$•7H$_2$O dissolved in 75 ml of H$_2$O [D’Ans and Freund, 1957]. The HOCl was purified by vacuum distillation and was stable over periods
of weeks when stored at dark at 273 K. A flow of He 0.5 to 50 sccm is bubbled the 273 K solution.

Cl₂, HCl and HNO₃ were all introduced into the flow tube with the carrier gas from mixtures in He (0.1-1%). Cl₂ (99.5) and HCl (99%) are obtained from Matheson (99%). HNO₃ is collected from a 3:1 solution of H₂SO₄ (96 wt %) and HNO₃ (70 wt %).

5.2.4 Calibrations of the MBMS System

H₂O signals were calibrated over the temperature range of 190 to 230 K by depositing an ice film from H₂O vapor and calculating its vapor pressure from the relationship given by Jansco et al. [1970]. Figure 5.4 shows an example of the H₂O calibration curve: the slope of the line yields the enthalpy of sublimation for ice and is 50.24 kJ/mol, consistent with the reported value by Jansco et al. (50.99 kJ/mol). The detection limit was about 10⁻⁵ Torr for H₂O.

HNO₃ was introduced to the flow tube from a dilute mixture in helium (0.5%), and its concentration was determined either by observing the pressure rise in the flow system upon its addition, or by using a 10-sccm mass flow meter. An example of the HNO₃ calibration is given in Figure 5.5, showing the HNO₃ signal (by detection of the NO₂⁺ ion fragment at m/e = 46) as a function of its density. The mass spectrometer detection limit of HNO₃ was determined by the magnitude of NO₂⁺ background signal arising both from the flow tube and the sampling line and was typically about 10⁻⁸ Torr.

The calibrations for HNO₃ and H₂O were also checked by making a NAT film and measuring simultaneously its HNO₃ and H₂O partial pressures. As shown in Figure 5.6,
Figure 5.4 $\text{H}_2\text{O}$ calibration over the temperature range of 230 to 200 K. The slope of the line yields the enthalpy of sublimation of ice and is 50.24 kJ/mole.
Figure 5.5 Calibration of HNO₃ over the partial pressure range of 5x10⁻⁷ to 5x10⁻⁶ Torr.
Figure 5.6 HNO$_3$ vs. H$_2$O vapor pressures for an NAT film prepared at 220 K in the flow tube, verifying the H$_2$O and HNO$_3$ calibrations. The solid line is the 220 K isotherm for NAT from Hanson and Mauersberger [1988a].
measurements of HNO₃ and H₂O vapor pressures over the NAT film along a 220 K isotherm are similar to those reported by Hanson and Mauersberger [1988a] for NAT crystals. The measured slope of a log(HNO₃) versus log(H₂O) is -2.92, consistent with the NAT slope of -3, according to the Gibbs-Duhem equation discussed in section 3.1.1.

HCl, HOCl, and Cl₂ were monitored at mass peaks of 36, 52, and 70, respectively. Calibrations for those species were performed similarly as that for HNO₃. Detection limits were 10⁻⁸ Torr for HOCl and Cl₂. Due to the "sticky" nature of HCl the detection sensitivity was limited mainly by its background partial pressure, which was approximately 10⁻⁷ Torr.

ClONO₂ was calibrated using a ultraviolet spectrophotometer. The concentration of ClONO₂, prior to passing through a needle valve and entering the flow tube, was determined by UV absorption at 220 nm (cross section = 3.44x10⁻¹⁸ cm²) [Demore et al., 1990]. Typical detection limits in the UV absorption system at 220 nm were 3 x 10⁻³ Torr which upon dilution, corresponded to a partial pressure of 1 x 10⁻⁷ torr in the flow tube. The mass spectrometer detection limit of ClONO₂ (also by detection of the NO₂⁺ ion fragment at m/e = 46) was typically about 1 x 10⁻⁸ Torr.

During experiments, the mass spectrometer signals, the flows, the total pressure, and the temperature were simultaneously recorded by a computer data acquisition system.

5.3 Heterogeneous Interactions of ClONO₂ and HCl with Sulfuric Acid Tetrahydrate (SAT)

5.3.1 RESULTS
HCl Uptake Experiments

An important parameter for understanding the interaction between a molecule and a surface is the approximate surface coverage of the molecule. Uptake from the gas phase was determined from the decline and recovery in the HCl signal and the flow rates, i.e., the number of molecules lost is determined by monitoring the absolute gas-phase concentration while is exposed to the surface, and the initial concentration when it is not exposed to the surface. The time integrated difference between the two concentrations, when multiplied by the volume flow rate, yields the total number of molecules lost. The uptake of HCl by SAT films was studied using the method previously described [Hanson and Ravishankara, 1992; Abbatt and Molina, 1992; Abbatt et al., 1992]. Briefly, a steady state flow of HCl in helium was first established through one of the unjacketed injectors pushed in just pass the solid sulfuric acid film. The injector was then quickly pulled upstream exposing 3-10 cm length of the film to HCl while monitoring the HCl signal in the mass spectrometer.

Figure 5.7 shows time evolution of the HCl signal for two typical uptake experiments performed at 195 K and $P_{H2O} = 4 \times 10^{-4}$ Torr: the injector is pulled 5 cm upstream at 1.0 min, and returned to its original position at 3.0 min. For the case of the small HCl concentration ($\sim 6.7 \times 10^{-7}$ Torr) the HCl signal falls from its initial steady state value as HCl is taken up by the SAT film, and later returns as the surface layer becomes saturated with HCl; pushing back the injector results in HCl desorption, with a peak similar to the uptake peak (top trace). The total number of HCl molecules taken up is calculated to be $\sim 1.5 \times 10^{14}$ molecules cm$^{-2}$, corresponding to 15% of a monolayer coverage assuming a cross sectional area of 10 Å$^2$ for the adsorbed HCl molecules and a SAT surface area equal to the geometrical area of the flow tube. For the high
initial HCl concentration \((2 \times 10^{-5} \text{ Torr})\) the HCl signal drops substantially on pulling the injector upstream and does not recover to its starting level on the time scale of minutes, probably indicating that surface melting occurs (bottom trace).

The dependence of the HCl uptake on its gas phase concentration is illustrated in Figure 5.8 over the range of HCl concentrations from \(3 \times 10^{-7} \text{ Torr}\) to \(2 \times 10^{-5} \text{ Torr}\), showing the expected variability of HCl uptake as a function of HCl concentration, namely, increasing uptake with increasing concentration. The temperature and \(\text{H}_2\text{O}\) partial pressure are kept constant at 195 K and \(P_{\text{H}_2\text{O}} = 4.5 \times 10^{-4} \text{ Torr}\) during these experiments. A threshold HCl partial pressure, above which melting occurs, is identified at \(-1.5 \times 10^{-5} \text{ Torr}\) under those conditions.

Figure 5.9 shows results of the HCl uptake as a function of the \(\text{H}_2\text{O}\) partial pressure at 195 K and at a fixed HCl partial pressure of \(-5 \times 10^{-7} \text{ Torr}\). We have previously suggested that in an isothermal experiment a readjustment of the \(\text{H}_2\text{O}\) partial pressure in the flow tube is followed by a corresponding change in the thermodynamic state - and hence the composition - of the SAT film, occurring mostly in its surface layers. As shown in this Figure, the HCl uptake exhibits a strong dependence on the thermodynamic state of SAT: the \(\text{H}_2\text{O}\)-rich forms take up more than two orders of magnitude much HCl than the \(\text{H}_2\text{SO}_4\)-rich forms. When the \(\text{H}_2\text{O}\) partial pressure over the SAT film approaches that of pure ice, characteristic of the coexistence mixture of ice/tetrahydrate, the uptake resembles that observed on fresh ice films for the same temperature and HCl partial pressure conditions (open triangle, average of 9 experiments).

To simulate the temperature dependence of the HCl uptake under stratospheric conditions, we investigated the uptake by keeping the \(\text{H}_2\text{O}\) partial pressure constant and by varying the temperature in the flow tube, a process which also involves the transformation of \(\text{H}_2\text{O}\)-rich to
Figure 5.7 Time evolution of the HCl signal for two typical HCl uptake experiments on SAT at 195 K and \( P_{\text{H}_2\text{O}} = 4 \times 10^{-4} \) torr: (top trace) \( P_{\text{HCl}} = 6 \times 10^{-7} \) torr, and (bottom trace) \( P_{\text{HCl}} = 2 \times 10^{-5} \) torr. The injector is pulled upstream by 5 cm at 1 min, and returned to its original position at 3 min.
Figure 5.8 HCl surface coverages on SAT films as a function of $P_{\text{HCl}}$ at 195 K and $P_{\text{H}_2\text{O}} = 4.5 \times 10^{-4}$ torr. The solid curve is a fit of the experimental data in the form of equation (5.6) and is also summarized in Table 5.1.
Figure 5.9 HCl surface coverages on SAT films as a function of $P_{H_2O}$ at 195 K and $P_{HCl} \approx 5 \times 10^{-7}$ torr. Also shown in this figure is the result of HCl uptakes measured on fresh ice films (open triangle, average of 9 experiments). The ice vapor pressure at this temperature is labeled. The solid curve is a fit of the experimental data in the form of equation (5.6) and is also summarized in Table 5.1.
Figure 5.10 HCl surface coverages on SAT films as a function of temperature at $P_{H_2O} = 3.4 \times 10^{-4}$ torr and $P_{HCl} \approx 5 \times 10^{-7}$ torr. The ice frost point is labeled. The solid curve is a fit of the experimental data in the form of equation (5.6) and is also summarized in Table 5.1.
Table 5.1. Summary and Parameterization\(^a\) of the HCl Uptake Experiments

<table>
<thead>
<tr>
<th>Variable</th>
<th>Coefficients</th>
<th>Experimental Conditions</th>
</tr>
</thead>
<tbody>
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<td></td>
<td>(a_1)</td>
<td>(a_2)</td>
</tr>
<tr>
<td>(P_{\text{HCl}}) (Torr)</td>
<td>32.58</td>
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<td>(P_{\text{H2O}}) (Torr)</td>
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<td>7.79</td>
</tr>
<tr>
<td>(T) (K)</td>
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<td>7.99</td>
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\(^a\) \(\log S_{\text{HCl}} = a_1 + a_2 \log x + a_3 \log^2 x\)

\(S_{\text{HCl}}\) in molecules cm\(^{-2}\)
H$_2$SO$_4$-rich hydrate as the substrate is warmed from 192 to 218 K at the particular H$_2$O partial pressure of the experiment ($3.4 \times 10^{-4}$ Torr). Figure 5.10 gives the results of these experiments at a fixed $P_{\text{HCl}}$ ($\sim 6 \times 10^{-7}$ Torr) as a function of temperature. As shown in this Figure, at high temperatures ($T > 200$ K) the SAT film takes up only very small amount of HCl ($< 10^{13}$ molecules cm$^{-2}$) whereas the uptake approaches a tenth of a monolayer coverage ($\sim 10^{14}$ molecules cm$^{-2}$) at low temperatures ($T < 195$ K).

For convenience in presentation, the data shown in Figures 5.8, 5.9, and 5.10 are also summarized in Table 5.1: the surface coverage of HCl ($SC_{\text{HCl}}$) is fitted by the following functional form:

$$\log SC_{\text{HCl}} = a_1 + a_2 \log x + a_3 \log^2 x$$  \hspace{1cm} (5.6)

where $x$ can be replaced by $P_{\text{HCl}}$ (Torr), $P_{\text{H}_2\text{O}}$ (Torr), or $T$ (K); the coefficients $a_j$ ($j = 1, 3$) for each fit are tabulated along with the corresponding experimental conditions.

**Reaction of ClONO$_2$ with H$_2$O**

Reaction probabilities ($\gamma$) were calculated from first-order rate constants ($k$) corresponding to the reactant loss or product growth:

$$\gamma = 2rk/(\omega + rk)$$  \hspace{1cm} (5.7)

where $r$ is the radius of the flow tube and $\omega$ is the mean thermal speed of the reactant [Howard, 1979]. To account for the ClONO$_2$ radial gradients in the flow tube which arise when there is a large reactant wall loss, the observed first-order rate constants ($k_{\text{obs}}$) were corrected for gas diffusion by the method suggested by Brown to obtain $k$ [Brown, 1978]. The ClONO$_2$ diffusion
coefficient in helium used in the Brown calculations was 176 cm²/s at 200 K and 1 Torr, with a temperature dependency of $T^{4.76}$ and a pressure dependency of $P^{1}$, respectively [Hirshfelder et al., 1954]. These corrections were approximately 10% for small $\gamma$ values ($\gamma < 0.01$), and as large as a factor of 4 for large $\gamma$’s ($\gamma > 0.2$).

A typical experiment of reactive uptake of ClONO₂ by a SAT film is shown in Figure 5.11 as the time evolution of ClONO₂ and HOCI signals: at ~0.8 min, a 20-cm length of SAT film is exposed to ClONO₂ by pulling the injector upstream, and the concentration of ClONO₂ drops sharply to a very small value while the HOCI signal rises; at ~2 min, the injector is moved back downstream to stop the exposure and both the ClONO₂ and HOCI signals return instantly to their initial levels. As displayed in the figure, the product that leaves the surface is identified as HOCI; the other product, HNO₃, is left behind on the surface (HNO₃ is also detected by the $\text{NO}_2^+$ ion fragment at $m/e = 46$). In all of our experiments of this type, the maximum signal due to HOCI was always smaller than the initial ClONO₂ signal, suggesting some uptake of HOCI by the SAT surface. Since calibrations of the measured ClONO₂ and HOCI signals showed approximately the same relative sensitivities for detecting these two species in our mass spectrometer system, we estimated a lower limit of 50% for the yield of HOCI liberated into the gas phase.

Reaction probability ($\gamma_1$) measurements for the reaction between ClONO₂ and H₂O on SAT were conducted by observing the decay of ClONO₂ or the growth of HOCI as a function of the ClONO₂ injector position as it was pulled upstream over the SAT film. Figure 5.12 shows a semi-log plot of measured ClONO₂ and HOCI signals versus injector position for an experiment performed at 195 K and an initial ClONO₂ concentration of $7 \times 10^{-8}$ Torr. For the ClONO₂ decay
curve (top trace), the slope of the line yields the first-order rate constant; for the HOCI growth curve (bottom trace) the first-order rate constant is calculated from the slope of a plot of $(S_{\text{HOCI}}(\infty) - S_{\text{HOCI}}(z))$ versus injector distance, where $S_{\text{HOCI}}(\infty)$ is the HOCI signal at infinite reaction time and $z$ is the injector position. Both the ClONO$_2$ decay and HOCI growth follow first order kinetics. The difference in the reaction probabilities obtained using both methods is negligible within experimental precision.

In Figure 5.13, values of $\gamma_1$ calculated from experiments such as those displayed in Figure 5.12 are presented as a function of $P_{\text{H}_2\text{O}}$ at 195 K ($P_{\text{ClONO}_2} = (3 \text{ to } 5) \times 10^{-8}$ Torr). It is seen that as the H$_2$O partial pressure approaches that of pure ice, i.e., for H$_2$O-rich SAT, $\gamma_1$ approaches 0.016; for low H$_2$O partial pressures (H$_2$SO$_4$-rich SAT) its value decreases by almost two orders of magnitude. Also shown in this figure are results of $\gamma_1$ measurements performed on freshly prepared ice surfaces (open square, average of 15 experiments) and on HNO$_3$-treated ice surfaces (solid square, average of 11 experiments) at the same temperature.

To demonstrate the effect of temperature on $\gamma_1$ under conditions pertinent to the stratosphere, a set of experiments was conducted on SAT films at a fixed H$_2$O pressure ($P_{\text{H}_2\text{O}} = 3.4 \times 10^{-4}$ Torr) and over a range of temperatures. These results are depicted in Figure 5.14 with the ClONO$_2$ concentrations ranging from $(2 \text{ to } 4) \times 10^{-8}$ Torr. At high temperatures ($T > 205$ K), $\gamma_1$ is observed to be less than $10^{-3}$, whereas it increases substantially at low temperatures ($\gamma_1 > 0.02$ at $T < 195$ K).

The data for $\gamma_1$ displayed in Figures 5.13 and 5.14 are also parameterized in the form of equation (5.6), and the coefficients are given in Table 5.2 along with the experimental conditions.
Figure 5.11 Time evolution of ClONO$_2$ ($m/e = 46$) and HOCl ($m/e = 52$) signals for a typical ClONO$_2$ reactive uptake experiment on SAT. Experimental conditions: $P_{ClONO_2} = 7 \times 10^{-8}$ torr, $P_{H_2O} = 4 \times 10^{-4}$ torr, $P_{He} = 0.8$ torr, Velocity = 1371 cm s$^{-1}$, $T = 195$ K.
Figure 5.12 ClONO$_2$ (top trace) and HOCI (bottom trace) signals as a function of injector position. For the HOCI growth curve the first-order rate constant is calculated from the slope of a plot ($S_{\text{HOCI}}(\infty) - S_{\text{HOCI}}(z)$) (solid curve), where $S_{\text{HOCI}}(z)$ and $S_{\text{HOCI}}(\infty)$ are the HOCI signal at infinite reaction time (see text for details). Experimental conditions: $P_{\text{ClONO}_2} = 7 \times 10^{-8}$ torr, $P_{\text{H}_2\text{O}} = 5.4 \times 10^{-4}$ torr, $P_{\text{He}} = 1.0$ torr, Velocity = 1500 cm s$^{-1}$, $T = 195$ K.
Figure 5.13 Reaction probability ($\gamma_i$) for reaction (5.1) as a function of $P_{H_2O}$ on SAT surfaces at 195 K. Open circles are $\gamma_i$'s determined by ClONO$_2$ decay, and solid circles are determined by HOCl growth. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.2. Also shown in this figure are $\gamma_i$'s measured on fresh ice films (open square, average of 15 experiments) and on HNO$_3$-treated ice films (solid square, average of 11 experiments). The ice vapor pressure at this temperature is labeled. Experimental conditions: $P_{ClONO_2} = 3 \times 10^{-8} \rightarrow 5 \times 10^{-8}$ torr, $P_{He} = 0.9 \rightarrow 1.0$ torr, Velocity = 1300 \rightarrow 1500$ cm s$^{-1}$, $T = 195$ K.
Figure 5.14 Reaction probability ($\gamma_1$) for reaction (5.1) as a function of temperature on SAT surfaces. Open circles are $\gamma_1$'s determined by ClONO$_2$ decay, and solid circles are determined by HOCl growth. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.2. The ice frost point is labeled. Experimental conditions: $P_{\text{ClONO}_2} = 2 \times 10^{-8} \rightarrow 4 \times 10^{-8}$ torr, $P_{\text{H}_2\text{O}} = 3.4 \times 10^{-4}$ torr, $P_{\text{He}} = 0.9 \rightarrow 1.0$ torr, Velocity $= 1300 \rightarrow 1600$ cm s$^{-1}$, $T = 195$ K.
Table 5.2. Summary and Parameterization\(^a\) of the $\gamma_1$ Measurements

<table>
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<tr>
<th>Variable</th>
<th>Coefficients</th>
<th>Experimental Conditions</th>
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<td>$x$</td>
<td>$a_1$</td>
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<td>$P_{H2O}$ (Torr)</td>
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<td>$T$ (k)</td>
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<td>-3.13</td>
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\(^a\) \log \gamma_1 = a_1 + a_2 \log x + a_3 \log^2 x

$T = 195$ K
$P_{ClONO_2} = 3 \times 10^{-8} \rightarrow 5 \times 10^{-8}$ Torr
$P_{H2O} = 4 \times 10^{-4} \rightarrow 5.6 \times 10^{-4}$ Torr

$T = 192 \rightarrow 206$ K
$P_{ClONO_2} = 2 \times 10^{-6} \rightarrow 4 \times 10^{-8}$ Torr
$P_{H2O} = 3.4 \times 10^{-4}$ Torr

229
For all experiments described above, a freshly prepared SAT film was used for each measurement. Attempts were also made to examine the effect of flow tube radius on the $\gamma_1$ values: within experimental precision the results using the two flow tubes with different inner diameters were essentially the same. The estimated error limit of the $\gamma_1$ values is approximately $\pm 30\%$, which includes the uncertainties in measuring the first-order rate constant and in correcting the gas phase diffusion. It, however, does not include correction due to porosity and surface roughness, to be discussed below. Scatter of the $\gamma_1$ values may partially be attributed to the slight variation in ClONO$_2$ concentrations in different experiments.

**Reaction of ClONO$_2$ with HCl**

We investigated the reactive uptake of ClONO$_2$ by SAT in the presence of HCl vapor: the measurements were performed by allowing the substrate to equilibrate with HCl vapor introduced into the flow tube with helium through one of the unjacketed injectors.

Figure 5.15 shows the ClONO$_2$ and Cl$_2$ signals as a function of time for a typical experiment conducted at 195 K and at a H$_2$O partial pressure of 4x10$^{-4}$ Torr. The initial concentrations of ClONO$_2$ and HCl for this experiment are 7x10$^{-8}$ and 4x10$^{-7}$ Torr, respectively. At 1.4 min the ClONO$_2$ injector is pulled upstream by 8 cm and a pronounced time-independent decrease is observed in the ClONO$_2$ signal while the Cl$_2$ signal increases instantly. When the injector is pushed back to its starting position at 2.6 min, both ClONO$_2$ and Cl$_2$ return immediately to their original levels. No release of HOCl into the gas phase was observed during this process. Correcting the measured signals for relative sensitivities for detection of ClONO$_2$
and Cl₂ gave a Cl₂ yield of 0.9±0.1.

As is the case with the reaction between ClONO₂ and H₂O, γ₂ can be calculated both from the decay of the ClONO₂ signal and from the growth of Cl₂ as a function of the ClONO₂ injector position. In Figure 5.16, the first-order rate constant for Cl₂ rise (bottom trace) within the uncertainty of the measurement is essentially the same as that for the ClONO₂ loss (top trace).

Results for γ₂ measurements are shown in Figure 5.17 at 195 K as a function of the H₂O partial pressure. The temperature dependence of the γ₂ values is presented in Figure 5.18 for a constant H₂O partial pressure of 5.5x10⁻⁴ Torr. As shown in these figures, the H₂O-rich crystals show γ₂ values ≥ 0.1, whereas the γ₂ values for the H₂SO₄-rich crystals are more than two orders of magnitude smaller. Note that for the same reactant partial pressures the γ₂ on H₂O-rich SAT is ~0.1 at 195 K, and increases slightly at 190 K (> 0.2). The parameterized temperature and P_H₂O dependencies of γ₂'s for data shown in Figures 5.17 and 5.18 are listed in Table 5.3.

For all the experiments described above, initial concentrations of HCl were always higher than those of ClONO₂ so that the pseudo first-order assumption applies (P_{ClONO₂} = (3-5)x10⁻⁸ Torr and P_{HCl} = (4-8)x10⁻⁷ Torr). The uncertainty in the γ₂ values is approximately ±30% for γ₂ < 0.1; for larger γ₂ values (which are more sensitive to the gas-phase diffusion), the uncertainty is as large as a factor of 4. Some scatter in γ₂ (Figures 5.17 and 5.18) may also be due to variations in both ClONO₂ and HCl concentrations in the various experiments.

5.3.2 DISCUSSION

HCl Uptake Experiments
Figure 5.15 Time evolution of ClONO$_2$ ($m/e = 46$) and Cl$_2$ ($m/e = 70$) signals for a typical ClONO$_2$ reactive uptake experiment on SAT in the presence of HCl vapor. Experimental conditions: $P_{\text{ClONO}_2} = 7\times 10^{-8}$ torr, $P_{\text{H}_2\text{O}} = 4\times 10^{-4}$ torr, $P_{\text{HCl}} = 4\times 10^{-7}$ torr, $P_{\text{He}} = 1.3$ torr, Velocity = 1400 cm s$^{-1}$, $T = 195$ K.
Figure 5.16 ClONO$_2$ (top trace) and Cl$_2$ (bottom trace) signals as a function of injector position. For the Cl$_2$ growth curve the first-order rate constant is calculated from the slope of a plot ($S_{Cl_2}(\infty) - S_{Cl_2}(z)$) (solid curve), where $S_{Cl_2}(\infty)$ is the Cl$_2$ signal at infinite reaction time (see text for details). Experimental conditions: $P_{ClONO_2} = 7 \times 10^{-8}$ torr, $P_{H_2O} = 2.4 \times 10^{-4}$ torr, $P_{HCl} = 5 \times 10^{-7}$ torr, $P_{He} = 1.0$ torr, Velocity = 1571 cm s$^{-1}$, $T = 195$ K.
Figure 5.17 Reaction probability ($\gamma_2$) for reaction (5.2) as a function of $P_{H_2O}$ on SAT surfaces at 195 K. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.3. Open circles are $\gamma_2$'s determined by ClONO$_2$ decay, and solid circles are determined by Cl$_2$ growth. The ice vapor pressure at this temperature is labeled. Experimental conditions: $P_{ClONO_2} = 3 \times 10^{-8} \rightarrow 5 \times 10^{-8}$ torr, $P_{HCl} = 4 \times 10^{-7} \rightarrow 8 \times 10^{-7}$ torr, $P_{He} = 0.9 \rightarrow 1.0$ torr, Velocity $= 1300 \rightarrow 1600$ cm s$^{-1}$, $T = 195$ K.
Figure 5.18 Reaction probability ($\gamma_2$) for reaction (5.2) as a function of temperature on SAT surfaces. Open circles are $\gamma_2$'s determined by ClONO$_2$ decay, and solid circles are determined by HOCl growth. The solid curve is a fit to the experimental data in a functional form similar to equation (5.6) and is also summarized in Table 5.3. The ice frost point is labeled. Experimental conditions: $P_{\text{ClONO}_2} = 2\times10^{-8}$ to $5\times10^{-8}$ torr, $P_{\text{H}_2\text{O}} = 5.6\times10^{-4}$ torr, $P_{\text{HCl}} = 4\times10^{-7}$ to $8\times10^{-7}$ torr, $P_{\text{He}} = 0.9$ to $1.0$ torr, Velocity $= 1300$ to $1600$ cm s$^{-1}$, $T = 195$ K.
Table 5.3. Summary and Parameterization\(^a\) of $\gamma_2$ Measurements

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<td>$P_{\text{H}_2\text{O}} = 4 \times 10^{-5} \rightarrow 5.6 \times 10^{-4}$ Torr</td>
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<tr>
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<tr>
<td></td>
<td></td>
<td>$P_{\text{H}_2\text{O}} = 5.6 \times 10^{-4}$ Torr</td>
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\(^a\) $\log \gamma_2 = a_1 + a_2 \log x + a_3 \log^2 x$
There have been numerous investigations of the HCl interaction with proposed PSC materials [Moore et al., 1990; Leu et al., 1991; Hanson and Ravishankara, 1992; Abbatt and Molina, 1992; Abbatt et al., 1992; Hanson and Mauersberger, 1988; Wofsy et al., 1988; Elliott et al., 1990; Marti et al., 1991; Chu and Leu, 1993], with emphasis ranging from bulk HCl solubility to the HCl surface concentration. The nature of this process, however, is only recently beginning to be elucidated: HCl is only sparingly soluble in ice [Molina, 1993], but a significant amount of HCl vapor is taken up by the ice surface (corresponding to a fraction of a monolayer coverage under stratospheric conditions) [Hanson and Ravishankara, 1992; Abbatt et al., 1992; Chu and Leu, 1993]. Similar behavior is also observed for HCl uptake on NAT [Hanson and Ravishankara, 1992; Abbatt and Molina, 1992; Chu and Leu, 1993]. In addition, the thermodynamic state of NAT has been shown to strongly influence the HCl uptake [Abbatt and Molina, 1992].

As we have previously demonstrated, the thermodynamic state of SAT is determined by two variables, e.g., either by the H$_2$O partial pressure at a given temperature or by the temperature at a given H$_2$O partial pressure. The present data show that H$_2$O-rich SAT surfaces take up more HCl than H$_2$SO$_4$-rich surfaces, which is expected since the chemical potential of H$_2$O in H$_2$SO$_4$-rich surfaces is smaller than that in H$_2$O-rich surfaces. Hence, the tight H$_2$O bonding in the H$_2$SO$_4$-rich surfaces leads to fewer free H$_2$O molecules available to interact with HCl molecules. The results also show that at very high HCl concentrations ($P_{HCl} > 10^5$ Torr) unlimited uptake occurs without showing HCl saturation on the time scale of several minutes, suggesting that melting occurs. These observations are qualitatively similar to the reported HCl uptake behavior on NAT [Hanson and Ravishankara, 1992; Abbatt and Molina, 1992]. For the
HCl uptake by ice, our data are in reasonable agreement with the that reported by Hanson and Ravishankara [1992].

Theoretical considerations based on a physical adsorption mechanism predict HCl uptakes orders of magnitude smaller than observed on the ice surface [Molina, 1993; Kroes and Clary, 1992]. We have postulated an alternative mechanism involving the formation of a liquid-like layer and solvation of HCl on the ice surface, which is supported by thermodynamic considerations involving surface free energies [Molina, 1993]. By analogy, we believe that such a mechanism most likely accounts for the observed HCl uptake on SAT reported in this study. As is seen in Figure 5.8, the HCl uptake increases rapidly as $P_{\text{HCl}}$ approaches the "threshold" value for melting, which appears to indicate that the thickness of the liquid-like layer increases accordingly, as is the case with the liquid-like layer on ice as temperature approaches 0°C.

Leu et al. [1991] and Keyser et al. [1991] have shown that a porosity effect related to the thickness of the substrate may significantly affect the measured $\gamma$ values as well as the HCl uptake, a subject which is currently in debate [Hanson and Ravishankara, 1992; Keyser et al., 1993; Hanson and Ravishankara, 1993]. Because we prepared SAT films by wetting the flow tube with 57.8 wt % H$_2$SO$_4$ solution and by subsequent freezing, it was difficult to characterize the roughness and porosity of these SAT surfaces. Visually, the SAT films used in our experiments appeared smooth and uniform, and were likely to be less porous than ice films formed by H$_2$O vapor deposition. Our results indicate that the H$_2$O-rich SAT takes up essentially the same amount of HCl molecules as the ice film, despite the fact that these two types of surfaces were prepared in very different ways.
Reaction of ClONO$_2$ with H$_2$O

A wide variation of $\gamma_1$ measurements on ice surfaces has been reported in the literature, with $\gamma_1$'s ranging from 0.009 to $\geq$ 0.3 [Molina et al., 1987; Tolbert et al., 1987; Tolbert et al., 1988; Leu, 1988a,b; Hanson and Ravishankara, 1991; Hanson and Ravishankara, 1992]. This discrepancy was later resolved as due to the difference in ClONO$_2$ concentrations used in each of those studies [Hanson and Ravishankara, 1991]: high ClONO$_2$ concentrations in many of the early experiments led to surface saturation by HNO$_3$ (the reaction product) and caused deactivation of the ice surface. We also measured $\gamma_1$'s on fresh ice films at 195 K: for the ClONO$_2$ concentration range of $2 \times 10^{-8}$ to $1 \times 10^{-7}$ Torr, $\gamma_1$'s were found to be $0.08 \pm 0.02$ for an average of 15 experiments (Figure 5.13, open square). These values are noticeably smaller than those reported by Hanson and Ravishankara ($\geq 0.3$) [Hanson and Ravishankara, 1991; Hanson and Ravishankara, 1992], considering the same level of ClONO$_2$ concentrations used in both studies; they are, however, in good agreement with recent results obtained by Leu [1993].

We also performed some experiments by first exposing fresh ice films to ClONO$_2$ at $\sim 10^{-7}$ Torr on a time scale of several minutes and then measuring $\gamma_1$ on such a HNO$_3$-contaminated surface. It has been previously suggested that exposure of an ice film to ClONO$_2$ convert it to a HNO$_3$-doped surface, most likely in the form of NAT [Hanson and Ravishankara, 1991; Hanson and Ravishankara, 1992]. The $\gamma_1$'s we obtained on these surfaces were on the order of 0.002 (Figure 5.13, solid square), similar to the results of $\gamma_1$'s measured on H$_2$O-rich NAT [Abbatt and Molina, 1992].

It is interesting to note that for ice, H$_2$O-rich SAT, and H$_2$O-rich NAT the $\gamma_1$ values
decrease in that order (Figure 5.13). It is likely that the presence of HNO$_3$ and H$_2$SO$_4$ molecules in the surface layer is responsible for this behavior: as mentioned above, HNO$_3$ molecules in the NAT/ice coexistence mixture may deactivate the surface layer and, hence, slow reaction (5.1). Alternatively, the difference in the $\gamma_1$ values between ice and H$_2$O-rich SAT may be attributed to the difference in surface characteristics of the two types of films, i.e., the porosity effect as proposed by Leu et al. [1991] and Keyser et al. [1991] although this seems to be inconsistent with our observations of HCl uptake discussed above.

Our results show that $\gamma_1$'s depend strongly on the thermodynamic state of SAT (Figures 5.13 and 5.14): at a given temperature $\gamma_1$'s increase with increasing H$_2$O partial pressure; at a given H$_2$O partial pressure $\gamma_1$'s decrease with increasing temperature. This behavior is consistent with the HCl uptake discussed above, in terms of the reduced chemical potential of H$_2$O in H$_2$SO$_4$-rich substrate.

Lastly, there is some evidence indicating that $\gamma_1$ on H$_2$O-rich SAT increases slightly with decreasing temperature (see Figures 5.13 and 5.14). The same tendency was observed for the reaction between HOCl and HCl, [Abbatt and Molina, 1992] but the opposite behavior was reported for the $\gamma_1$ on H$_2$O-rich NAT [Hanson and Ravishankara, 1991].

**Reaction of ClONO$_2$ with HCl**

The $\gamma_2$'s also show a strong dependence on the thermodynamic state of SAT (Figures 5.17 and 5.18), similar to that found in the HCl uptake and $\gamma_1$ experiments. For H$_2$O-rich SAT our measured $\gamma_2$'s are compatible with the large $\gamma_2$ values reported on H$_2$O-rich NAT [Hanson
and Ravishankara, 1992; Abbatt and Molina, 1992]. We also observed that $\gamma_2$ on H$_2$O-rich SAT slightly increases with decreasing temperature for the same reactant partial pressures ($\gamma_2 = 0.12$ at 195 K and $\gamma_2 \geq 0.3$ at 190 K).

It was previously suggested that on water-ice and H$_2$O-rich NAT reaction (5.2) involves a two-step process which consists of reaction (5.1) followed by reaction (5.3) [Hanson and Ravishankara, 1992; Abbatt and Molina, 1992]. We believe that such a process also applies for reaction (5.2) on SAT: both reduced HCl surface concentrations and small $\gamma_1$'s for H$_2$SO$_4$-rich SAT lead to the reduced $\gamma_2$'s; reaction (5.3) enhances $\gamma_2$ by refreshing the SAT surface with H$_2$O. We have recently proposed that a more realistic mechanism for reaction (5.6) includes the following ionic reaction, which occurs after HCl uptake and solvation in the liquid like layer.

Additional experiments to elucidate this mechanism is discussed below.

5.3.3 STRATOSPHERIC IMPLICATIONS

Our early studies have shown that SAT may form and persist at temperature and H$_2$O partial pressure conditions typical of the high-latitude stratosphere: once crystallized, those aerosols are stable until they melt at ~215 K or are removed from the stratosphere by scavenging or by acting as condensation nuclei in the formation of PSCs. These studies also suggest that in the stratosphere, considering a constant ambient H$_2$O mixing ratio, the thermodynamic state of frozen sulfate aerosols is determined only by temperature. For most of experiments reported here, the gas phase HCl and ClONO$_2$ concentrations are maintained at levels that are representative of the stratosphere, and hence the measurements are directly applicable to the
stratosphere.

Our results show that at an ambient stratospheric H₂O partial pressure of 3.4×10⁻⁴ Torr (∼5 ppmv H₂O mixing ratio at 100 mb) HCl uptake by frozen sulfate aerosols approaches a tenth of a monolayer coverage (∼10⁻¹⁴ molecules cm⁻²) at low temperatures (T < 195 K) whereas only a very small amount of HCl (< 10⁻¹² molecules cm⁻²) is taken up at temperatures higher than 200 K. For reaction (1) γ₁ is observed to be on the order of 0.02 at low temperatures (T < 195 K), and less than 0.002 at temperatures above 205 K. Similarly, γ₂ is found to be greater than 0.2 at low temperatures (T < 195 K), and decreases substantially with increasing temperature. These results imply that in the stratosphere the heterogeneous interactions between ClONO₂ and HCl on frozen sulfate aerosols are largely governed by the temperature: they proceed efficiently at low temperatures (T < 195 K), and less efficiently when the temperature is higher (T > 205 K). Hence, chlorine activation should occur readily on frozen sulfate aerosols in the winter polar stratosphere, even in the absence of PSCs.

5.4 Mechanism of the Heterogeneous Reactions

Through much effort has been put into understanding the kinetics or heterogeneous reactions on the various proposed PSC materials, the reaction mechanism at the molecular level remains unclear.

Under stratospheric conditions, homogeneous gas phase chemistry can not explain the large ozone depletion observed in the polar spring [Molina et al., 1985; Friedl et al., 1986; Leu et al., 1989]. It is now recognized that the surfaces of PSC particles catalyze chemical
transformations, converting photoinactive chlorine reservoir into photoactive reservoir, via, for instance, reactions (5.2) and (5.3). For these reactions to proceed efficiently, HCl first needs to be available at the surface of PSC in sufficient amounts. Recent laboratory studies reveal that HCl is only sparingly in the proposed PSC materials, but a significant amount of HCl vapor is taken up on their surfaces, corresponding to a fraction of a monolayer coverage under stratospheric conditions [Hanson and Ravishankara, 1992; Abbatt and Molina, 1992; Chu et al., 1993].

The nature of interaction of HCl with surfaces of PSC particles has been a subject of several recent investigations, among which assumes molecular adsorption of HCl at the surfaces of the solid particles based on a Langmuir adsorption isotherm, competition for active sites, etc. [Elliott et al., 1991; Mozurkewich, 1993]. However, classic trajectory calculations based on physical adsorption yield HCl surface coverage on single ice crystals orders of magnitude smaller than the values observed experimentally [Kroes and Clary, 1992]. Thus the interpretation of HCl uptake by ice as being physically adsorbed is highly questionable. We have recently proposed that a liquid-like layer may form on the surfaces of PSC particles, in which HCl solvation occurs [Molina, 1993; Molina et al., 1993]. Here we present laboratory experiments to elucidate this particular mechanism.

We investigated the interaction of deuterium chloride with H₂O on ice, NAT, and SAT at 195 K and at DCl partial pressure of ~10⁻⁷ Torr,

\[ \text{DCl} + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{HOD} \]  \hspace{1cm} (5.8)

Such a bimolecular conversion requires first dissociation of DCl into to ions and subsequently undergoing ionic exchange with water, which is known to be extremely facile in liquid solutions.

243
Without DC1 solvation this reaction would be improbable, since the enthalpy for breaking the DC1 bond is as high as 103 kcal/mole [Lide, 1993].

The experimental apparatus was previously described in section 5.2. DC1 was eluted from a 9 molar DC1/D2O solution in a bubbler maintained at the dry-ice/acetone temperature. A typical mass spectrum of the effluent from the bubbler before exposure to a solid film is given in Figure 5.19, showing the characteristic DC1 peaks (m/e 37 and 39) along with the impurity peaks due to HCl (m/e 36 and 38). The HCl content can be attributed to contamination of the DC1 dose via H-D exchange in the gas handling lines; this should not affect the results.

The reaction of DC1 with H2O on ice, NAT and SAT was studied by first establishing a steady-state flow of DC1 in He (0.5 to 10 sccm) through one of the injectors pushed in just pass the solid film. The injector was then quickly withdrawn to an upstream location while both the DC1 and HCl signals were simultaneously monitored in the mass spectrometer. As shown in Figure 5.20, upon pulling the injector the HCl signal falls from its initial value as HCl is taken up by the ice film and later returns as the surface layer becomes saturated with HCl, consistent with the normal HCl uptake behavior observed in section 5.3.1. However, the concentration of HCl increases beyond what was being added from the injector at t > 6 min and reaches a steady state value at t > 15 min. The DC1 signal, on the other hand, drops to a low value upon pulling the injector upstream and remains low. Note that the increase in the HCl concentration at the steady state relative to its initial concentration (ΔHCl) is compatible to the decrease in the DC1 concentration (ΔDC1), indicating that adsorbed DC1 undergoes complete H-D exchange on the ice film. Experiments carried out on H2O-rich NAT and SAT at the same experimental conditions resemble that performed on ice.
The reaction of DCl with H$_2$O was also examined on NAT and SAT surfaces with different thermodynamic state or composition. As depicted in Figure 5.21, the exchange is evident on H$_2$SO$_4$-rich SAT with a H$_2$O partial pressure of 1.7x10$^{-4}$ Torr at 195 K (corresponding to 30% of the ice vapor pressure at that temperature or relative humidity). Again, the loss of DCl on the SAT film is almost equal to the rise of HCl, suggesting a nearly-complete conversion. The interaction of DCl with H$_2$O on HNO$_3$-rich NAT behaves similarly.

The occurrence of H-D exchange as displayed in Figures 5.21 and 5.21 is an intriguing result and demonstrates that DCl (HCl) can well be dissociatively adsorbed on the surfaces of all proposed PSC particles under stratospheric conditions. From a chemical binding point of view, solvation of HCl is unlikely in the absence of the liquid-like layer, because the orientation and mobility of H$_2$O molecules are rather limited. The energy involved in the physical adsorption should be at most 7 kcal/mol, corresponding to the formation of a strong hydrogen bond between HCl and the surface. The consequence of such a small interaction energy would be the incorporation of negligible amounts of HCl under stratospheric conditions [Kroes and Clay, 1992]. The formation of a liquid-like layer, on the other hand, may involve modification of the surface layer in the presence of HCl, which may greatly increase the mobility of H$_2$O molecules. Subsequently, the adsorbed HCl molecules will be completely surrounded by water molecules with appropriate orientation, leading to dissociation of HCl with a release of energy of about 18 kcal/mol. This solvation energy is large enough to explain the experimentally observed HCl uptake results. The drastic surface rearrangement of ice crystals induced by adsorbates was previously documented by Orem and Adamson in the case of hydrocarbons, resulting in an adsorption process similar to that on liquid water [Orem and Adamson, 1969].
Complete dissociation of HCl on acid-rich SAT (or NAT) is also anticipated on thermodynamic grounds, since the stoichiometric ratio of water to acid is still very close 4:1 (or 3:1) for acid-rich SAT (or NAT). Furthermore, the observed HCl uptake on the acid-rich forms of NAT and SAT corresponds to a coverage on the order of $10^{-3}$ monolayer observed by this study and by Abbatt and Molina [1992], considerably larger than that theoretically predicted on single ice surface assuming physical adsorption ($10^{-7}$ monolayer) [Kroes and Clary, 1992].

The formation of the liquid-like layer on ice surface is further supported by our electrical conductivity measurements. The experimental apparatus has been described in section 3.2.2. High surface area ice sample ("powder ice") was prepared by first generating water droplets at room temperature with an ultrasonic nebulizer. The particles were suspended in a stream of air, which was directed into a liquid nitrogen container. Ice particles with a mean diameter of about 4 $\mu$m were then collected and exposed to HCl vapor at a partial pressure of $\sim 10^{-5}$ Torr at 200 K on the time scale of several minutes. Figure 5.22 illustrates the conductance variation with temperature when cooling the sample down to 150 K and subsequent warming. As is seen in this figure, minor amounts of liquid HCl on the surfaces of the ice particles persist at temperatures as low as 165 K upon cooling. The liquid forms as a result of surface melting, which may have higher HCl vapor pressure than that found in the stratosphere, discussed in section 3.4. However, if a liquid-like layer consisting of several layers, a film with an HCl concentration of 10-20 wt % may well form under stratospheric conditions.

In a recent study, the apparent lack of H-D exchange from temperature-programmed reaction of HCl with thin D$_2$O film at 150 K is reported and, it is consequently postulated that HCl adsorption is in a molecularly adsorbed state [Roberts and Graham, 1993]. Another similar
study using reflection-adsorption infrared spectroscopy, however, observed no H-Cl stretching
frequency on thin D₂O ice films at 110 K and suggest that HCl adsorption is entirely dissociative
[Horn et al., 1992]. The reason for the apparent discrepancy between the two studies is unclear.
We note, however, that these experiments were performed at extremely cold temperatures, which
are not directly applicable in the stratosphere. Indeed, amorphous solid HCl solutions may form
at these temperatures, as discussed in section 3.4. Also, using Fourier-transform infrared
spectroscopy, Koehler et al. [1993] could not detect any HCl uptake by ice films at temperatures
close to those found in the stratosphere. Based on the analysis of earlier laboratory studies,
Tabazadeh and Turco [1993] conclude that a liquid layer may form on surfaces of ice and H₂O-
rich NAT with complete HCl dissociation. Their general conclusion is consistent with our
observations. However, for HNO₃-rich NAT they obtain an HCl adsorption energy roughly 5
kcal/mol lower than our observations. In fact, the application of the BET adsorption isotherm
in their study may have limitations. For example, the BTE adsorption isotherm predicts an
increased number of adsorbed water layers with decreasing temperature on the ice surface,
contrary to the notion that liquid-like layers on ice diminish with decreasing temperature,
investigated extensively in the literature [Hobbs, 1974; Kuroda and Lacmann, 1982; Furukawa
et al., 1987]. Also, the HCl concentration in the liquid layer resulting from their model is so
high that such a film would be unstable under stratospheric conditions. Chu et al. [1993] recently
reported that HCl surface coverage on ice was proportional nearly to the second power of the
HCl vapor pressure, indicating that HCl dissociation could have taken place. The interpretation
given by Chu et al. [1993] applies only to homogeneous solutions; this point merits further
confirmation.
It has been suggested that on water-ice, NAT, and SAT reaction (1) involves a two-step process, which is initiated by ClONO$_2$ hydrolysis followed by reaction (2) [Hanson and Ravishankara, 1992; Abbatt and Molina, 1992]. Our results indicate that the mechanism for reaction (2) is the same on various proposed PSC surfaces: it involves the formation of a liquid-like layer on the solid surfaces and subsequent dissociation of HCl. Consequently, reaction (2) is surely ionic, proceeding essentially without activation energy

\[ \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) + \text{HOCl(aq)} \rightarrow \text{Cl}_2(\text{gas}) + \text{H}_2\text{O(liq)} \]  

(5.9)

Eigen and Kustin [1960] investigated this reaction at 198 K; its rate is likely to be close to the diffusion-limit in the liquid-like layer, which is highly acidic. This mechanism may well be operable on the surfaces of PSC particles.
Figure 5.19 Mass Spectra of the DCI bubbler effluent before exposure to a solid film.
Figure 5.20 Interaction of DCl with H$_2$O on an ice film at 195 K: at 0.8 min, a 5-cm length of the ice film is exposed to DCl by pulling the injector upstream; at 5 min, the injector is moved back to its original position to stop the exposure. Both HCl and DCl signals return to their initial concentrations upon pushing back the injector.
Figure 5.21 Interaction of DCl with H₂O on H₂SO₄-rich SAT with a H₂O partial pressure of 1.7x10⁻⁴ Torr at 195 K (corresponding to 30% relative humidity).
Figure 5.22 Conductance variation with temperature for an HCl-doped power ice sample. The sample appeared dry and visually showed no sign of liquidation after being exposed to HCl vapor. The drop in the electrical conductivity upon warming to 173 K suggests that HCl migrates into the bulk to form a distinct H₂O-HCl phase in the form of HCl•6H₂O, as evident by the melting temperature at 198 K, corresponding to the ice/hexahydrate eutectic, discussed in section 3.4.3.
Chapter 6

Conclusions

This thesis presents laboratory studies of heterogeneous chemistry, which are important to understand phase properties and compositions of stratospheric particulate, the chemical reactivity on proposed aerosol stratospheric materials, and the mechanisms of PSC formation and heterogeneous reactions.

The physical chemistry of the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$, $\text{HNO}_3/\text{H}_2\text{O}$, and $\text{HCl}/\text{H}_2\text{O}$ binary systems is investigated under conditions pertinent to the stratosphere. The measurements include thermodynamic properties such as melting points, enthalpies of fusion, and vapor pressures and infrared spectra of liquid and supercooled solutions, and of liquid-solid and solid-solid coexistence mixtures of those acid systems. The data reveal that some hydrates of $\text{H}_2\text{SO}_4$ (i.e., $\text{H}_2\text{SO}_4\cdot4\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot6.5\text{H}_2\text{O}$, $\text{H}_2\text{SO}_4\cdot8\text{H}_2\text{O}$) may form and persist under in the stratosphere. The melting experiments demonstrate that SAT melts at 215 K under stratospheric conditions. Thus, crystalline sulfuric acid hydrates may be an important component of the stratospheric sulfate layer, particularly at high-latitude. HCl hydrates, on the other hand, are concluded to be unstable in the stratosphere. Thermodynamics and phase equilibria for the binary systems are discussed. Thermodynamic properties such as enthalpies of formation for pure crystalline
hydrates as well as the corresponding liquid compositions are collaborated using the present and literature data. A method for describing solid-solid phase equilibria in a binary system, based on chemical equilibrium principles, is developed and compared with the experimental data for thermodynamic consistency.

HCl and HNO$_3$ solubilities in H$_2$SO$_4$ solutions are investigated in order to predict incorporation of stratospheric acids into background sulfate aerosols. From the data, Henry's law solubility constants for those systems are determined and equilibrium compositions of aqueous stratospheric aerosols are predicted as a function of ambient temperature and mixing ratios of H$_2$O, HNO$_3$, and HCl. The results indicate that at low temperatures characteristic of the stratosphere at high latitudes in the winter and spring, the HNO$_3$ content reaches the levels of the order of 10 wt % in the background sulfate aerosols. The present study also shows that the amount of HCl dissolved in liquid stratospheric aerosols is small when compared with the amount of HNO$_3$ dissolved. This is consistent with the in situ measurements of Pueschel et al. [1989; 1992], suggesting that only the most dilute fraction of the background aerosol is able to absorb HCl in amounts that allow deductibility by their instrument. On the other hand, at low temperatures chlorine activation is likely to be important through the surface reaction between ClONO$_2$ and dissolved HCl in the liquid aerosol droplets: our results show that for typical stratospheric HCl mixing ratios a nominal 38 wt % H$_2$SO$_4$ and 12 wt % HNO$_3$ droplet at 196 K takes up about 0.1 wt % HCl. This amount is large enough for chlorine activation to proceed at significant rates, as suggested previously by Wolff et al. [1989] and as indicated by experiments in our laboratory [Molina et al., 1993].

The solubility of HNO$_3$ in dilute H$_2$SO$_4$ solutions may be crucial for the formation and
growth of type I PSCs. As the stratosphere cools, HNO₃ and H₂O vapors condense on the liquid sulfuric acid droplets, forming increasingly dilute supercooled H₂SO₄/HNO₃/H₂O solutions. These solutions may freeze at low temperatures, with the possibility of forming various sulfuric acid hydrate crystals and NAT crystals; the later are clearly efficient type I PSC condensation nuclei. The identity of crystallized H₂SO₄/HNO₃/H₂O ternary solutions is examined from the vapor pressure measurements, along with infrared spectroscopic and DSC data performed in our laboratory, showing that indeed freezing of the supercooled H₂SO₄/HNO₃/H₂O solutions leads to the formation of a solid mixture consisting of nitric acid trihydrate (NAT) crystals and sulfuric acid tetrahydrate (SAT) crystals. A new mechanism for type I PSC formation is proposed and shown to reconcile many atmospheric observations.

A high sensitivity molecular beam (modulated) quadrupole mass spectrometer coupled to a fast-flow reactor is employed to study heterogeneous reactions on various proposed PSC materials. Measurements of the heterogeneous interactions of ClONO₂ and HCl on sulfuric acid tetrahydrate surfaces are made. The results indicate that the reaction probabilities of ClONO₂ with H₂O and HCl as well as the HCl uptake depend strongly on the thermodynamic state of the SAT substrate, with the H₂O-rich forms being more reactive than H₂SO₄-rich forms. In the stratosphere these reactions should proceed efficiently at low temperature (T < 200 K) and, hence, play an important role in chlorine activation in the winter polar stratosphere.

Finally, the mechanism of heterogeneous reactions is investigated. The present results constitute the first direct experimental observation for the formation of a liquid-like layer on the proposed PSC materials. The results reveal that the heterogeneous reaction between HOCl and HCl is ionic, proceeding essentially without activation energy.

255
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257


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265
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