Physical Chemistry of Acid Systems Relevant to Stratospheric Ozone Depletion

by

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B.S., Massachusetts Institute of Technology (1993)

Submitted to the Department of Earth, Atmospheric and Planetary Sciences

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Abstract

Thermodynamic properties of various binary $H_2SO_4/H_2O$, $HNO_3/H_2O$ and
$HCl/H_2O$ as well as ternary $H_2SO_4/HNO_3/H_2O$ solutions were studied using dif-
fferential scanning calorimetry. Stable as well as metastable hydrates were identified.
The supercooling trend of the solutions was also studied for both bulk and small
samples. In general, $H_2SO_4/H_2O$ solutions supercooled more readily than the other
binary solutions, suggesting that $H_2SO_4/H_2O$ solutions are in liquid form in the
stratosphere.

A time study was also conducted to investigate the likelihood that various ternary
solutions ($H_2SO_4/HNO_3/H_2O$) would freeze. Binary $H_2SO_4/H_2O$ and $HNO_3/H_2O$
solutions were also studied to compare freezing probabilities of these binary solutions
to the ternary solutions under the same equilibrium stratospheric conditions. A PSC
formation mechanism in which NAT crystallizes out first is introduced based on results
from this time study.

Finally, an experiment has been designed to study heterogeneous reactions on
a liquid surface and measure vapor pressures of various solutions. The apparatus
consists of a wetted-wall flow tube in conjunction with a molecular beam mass spec-
trometer. Preliminary data is presented to ensure the feasibility of the experiment.

Thesis Supervisor: Mario J. Molina
Title: Martin Professor of Atmospheric Chemistry
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Peace I leave with you; my peace I give you. I do not give to you as the world gives. Do not let your hearts be troubled and do not be afraid.

(John 14:27)

I pray that I will always strive to glorify His name in all my academic and personal endeavors.
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Chapter 1

Introduction

Ozone is the central species in stratospheric chemistry. Although its ambient concentration does not exceed 10 ppmv it is crucial to human life and other ecosystems because of its ability to strongly absorb biologically harmful ultraviolet radiation. This absorption of UV radiation by ozone contributes to the atmospheric temperature structure and thus, greatly affects meteorological processes. Its production and destruction are governed by the Chapman mechanism [65]:

\[ O_2 + h\nu (175 - 130 \text{ nm}) \rightarrow O + O \]

\[ O + O_2 + M \rightarrow O_3 + M \]

\[ O_3 + h\nu (240 - 290 \text{ nm}) \rightarrow O + O_2 \]

\[ O + O_3 \rightarrow 2O_2 \]

Although most ozone is photochemically produced in the tropical troposphere, transport to the lower stratosphere in the higher latitudes and its accumulation there due to slow vertical mixing cause the largest total ozone column amounts to occur near the polar stratospheres [65].
1.1 Chlorofluorocarbons

In recent decades, extensive research revealed the impact of human activities on the earth’s atmosphere. In particular, chlorofluorocarbons (CFCs) were shown to pose a threat to stratospheric ozone [34]. CFCs were developed by Thomas Midgley in 1930 and have become widely used as refrigerants, blowing agents for making foam, cleaning fluids, and propellants. They are ideal industrial chemicals because of their low boiling points, specific heats, heats of vaporization, surface tensions, and viscosities. Because they are non-toxic and non-flammable, CFCs are safe to use in a variety of consumer applications [42].

Unfortunately, the aspects that make them ideal industrial chemicals have disastrous effects. Once emitted into the atmosphere, these stable CFCs are relatively inert and have lifetimes ranging from 60 - 522 years [67]. Once in the upper stratosphere, they are removed photochemically [11]:

$$CF_2Cl_2 + h\nu (170 - 260 \text{ nm}) \rightarrow CF_2Cl + Cl$$

This photolysis occurs mainly in the “window” of 190 - 210 nm between the more intense absorption of the Schumann-Runge region of $O_2$ and the Hartley bands of $O_3$ [44].

1.2 Previous Theories Explaining Ozone Depletion

The discovery of the ozone “hole” in 1985 revealed that the total ozone column density over Antarctica had decreased by up to 50 %, but only during the austral spring [10]. This spurred extensive research to explain the cause of this hole. Several dynamical as well as chemical theories emerged, the most prominent ones being the dynamical, solar cycle and CFC theories.
1.2.1 Meteorology of Ozone Depletion

Before describing the theories explaining ozone depletion, the unique meteorological aspects of the high latitudes must be understood. After the autumnal equinox, the polar regions become dark and solar heating stops. The stratosphere begins to cool by infrared emission from $CO_2$. A latitudinal pressure gradient develops between the pole and mid-latitudes. Combined with the earth’s rotation, this pressure difference produces a circumpolar belt of westerly winds called the polar vortex. Wind speeds can reach up to 100 m/s and temperatures drop to as low as -80°C [46].

Differences between the two poles arise as a result of topographical variations. In the Northern Hemisphere, great mountain masses force Rossby waves to the stratosphere where thermal transport causes the vortex to be substantially warmer than its southern counterpart. This temperature difference explains the abundance of polar stratospheric clouds (PSCs) in the Antarctic vortex and the relative absence of PSCs in the Arctic [46].

1.2.2 Dynamical Theory

The most prominent purely dynamical theory to explain ozone depletion was introduced in 1986 by K. K. Tung and rested on the fact that warm air rises. Tung argued that there is another, much larger ozone hole over the tropics which is caused by a dynamical upwelling due to the low temperatures in the tropical lower stratosphere. While photochemistry predicts a maximum ozone concentration at the equator, the actual observed distribution of ozone demonstrates the need for including dynamic transport. With this in mind, Tung explained polar stratospheric ozone depletion in the following manner. When the sun returns to the polar region in the austral spring, absorption of ultraviolet radiation by ozone causes the heating rate to increase. As a result the local warmer air causes an upwelling and ozone-poor air from the tropics replaces the stratospheric ozone-rich air [56].

Since 1979, large amounts of aerosols have been injected into the atmosphere due to volcanic eruptions. Tung asserted that this could have resulted in a perturbation
in the overall climate and thus, dramatically affect column ozone amounts during the past decade [56]. Other possibilities may also exist: changes in heating rates following the systematic trends in sea surface temperatures which have been observed in recent years or changes due to the changing concentrations of infrared absorbers such as $CO_2, N_2O, CH_4, CF_2Cl_2, CFC_1_3$, etc. [43].

Using a two-dimensional circulation model, J.A. Pyle examined the effect of an increased heating rate on the polar ozone column. It revealed that if additional heating is introduced just before the end of the southern hemisphere polar night, the time scales are such that appreciable ozone changes do not occur for at least three months. Since the observed ozone loss occurs immediately upon the end of the polar night, Tung’s dynamical theory seemed implausible [43].

In addition to inconsistencies with modeling results Tung’s dynamical theory was also found to be inconsistent with the detailed vertical structure of the observed depletion and the chemical composition within the polar vortex itself. In studies the polar vortex exhibited a downward as opposed to an upward motion and while one would expect to see increasing amounts of upward diffusing species and decreasing amounts of downward diffusing species, such compositional variations were not observed to support his theory [47]. Thus, the dynamical theory was disproved.

1.2.3 Solar Cycle Theory

The solar cycle theory was put forth by Callis and Natarajan in 1986. The basis of this theory was the early-1970s finding that reactive nitrogen compounds ($NO$ and $NO_2$, known collectively as $NO_x$) can destroy ozone catalytically. Approximately every 11 years an increased solar flux results in an abundance of electrons in the atmosphere which, in the presence of $N_2$ and $O_2$, produce $NO_x$. Callis and Natarajan asserted that the recent ozone depletion phenomenon coincided with solar cycle 21, which occurred from 1978-1980, and thus, could be explained by $NO_x$ catalysis. They explained the ozone phenomenon in the following manner. In the vortex $NO$ and $NO_2$ react with ozone to produce $O, O_2$ and $NO_3$. $NO_2$ and $NO_3$ then react to form $N_2O_5$. When the sun returns in the spring, $N_2O_5$ and $NO_3$ undergo photolysis to form $NO_2$, which
then reacts with $O_3$ and depletion occurs [6].

If this theory were to hold true, $NO_x$ levels should be high in the polar vortex. Observations by Fahey et al. in 1989 showed that the opposite held true - $NO_x$ abundance was very low in the Antarctic vortex relative to lower latitudes. In general, it was found that the level of nitrogen-containing species was much lower inside the polar vortex [9]. In addition Mount et al. revealed that most of the $NO_x$ is at high altitudes (50 mb, or 25 - 30 km) whereas most of the ozone depletion occurs at lower altitudes (15 - 20 km) [38]. These findings disproved the solar cycle theory.

### 1.3 CFC Theory

The CFC theory of ozone depletion is currently accepted as the one which accurately explains the annual ozone hole. With the increase in anthropogenically released $Cl$ from CFCs in the stratosphere, Molina and Molina proposed the catalytic $ClO$ dimer mechanism to explain the loss of ozone [32]:

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

\[
(ClO)_2 + h\nu \rightarrow Cl + ClOO \tag{1.2}
\]

\[
ClOO + M \rightarrow Cl + O_2 + M \tag{1.3}
\]

\[
2(Cl + O_3) \rightarrow 2(ClO + O_2) \tag{1.4}
\]

\[
Net: 2O_3 \rightarrow 3O_2
\]

A synergistic $Cl - Br$ mechanism also describes $O_3$ loss [30]:

\[
ClO + BrO \rightarrow Cl + Br + O_2 \tag{1.5}
\]

\[
Cl + O_3 \rightarrow ClO + O_2 \tag{1.6}
\]

\[
Br + O_3 \rightarrow BrO + O_2 \tag{1.7}
\]
Net: $2O_3 \rightarrow 3O_2$

It is believed that 95% of the chemically catalyzed ozone loss can be explained by these chemical schemes: approximately 70% of the loss results from the $ClO$ dimer mechanism while the remainder is due to the $Cl - Br$ catalysis.

Traditional gas phase chemistry cannot account for the extent of the ozone depletion. Earlier satellite observations by McCormick et al. revealed that the Antarctic stratosphere is a region of extensive cloud formation [29]. Recently several researchers have linked stratospheric ozone loss to PSCs. Solomon et al. [48] and McElroy et al. [30] proposed heterogeneous reaction schemes to further explain ozone loss. This link to PSCs was a crucial one with which the ozone-depleting process could be explained in its entirety.

The following heterogeneous reaction scheme was proposed to occur on PSC particles:

\[
ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \tag{1.8}
\]
\[
ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \tag{1.9}
\]

These heterogeneous reactions have two important consequences: $Cl$ activation and $NO_x$ deactivation. By converting the stable $Cl$ reservoirs $ClONO_2$ and $HCl$ to the photo-sensitive forms of $Cl_2$ and $HOCl$, $Cl$ radicals are generated upon return of the sun in the early spring to begin the catalytic ozone destruction process. The conversion of $NO_x$ from $ClONO_2$ to the stable reservoir $HNO_3$ also encourages this catalytic cycle. Without $NO_x$, $Cl$ radicals are unable to return to their stable reservoir forms and as a result, they continue to freely destroy ozone molecules.

Molina et al. were the first to experimentally show that Reactions 1.8 and 1.9 were greatly enhanced in the presence of ice. Their results demonstrated that $Cl_2$ is released into the gas phase while $HNO_3$ remains in the condensed phase. Hence, Reactions 1.8 and 1.9 establish the necessary conditions for the efficient catalytic destruction of ozone by halogenated free radicals [35]. Tolbert et al. studied analogous reactions [52]:

\[
N_2O_5 + H_2O \rightarrow 2HNO_3 \tag{1.10}
\]
Again, Reactions 1.10 and 1.11 were enhanced in the presence of ice and supported Cl-catalyzed ozone destruction by $NO_x$ removal ($N_2O_5$ photodissociates to $NO_2$ and $NO_3$) and Cl-activation ($ClNO_2$ is photosensitive). Stratospheric clouds could clearly play an important role in ozone depletion.

### 1.4 Stratospheric Aerosols

Until recently, the only kind of stratospheric cloud thought to exist was the mother-of-pearl clouds (MPCs), or nacreous clouds. These are created by the sudden cooling and condensation of water vapor at altitudes of about 15 - 30 km. Because of the extreme dryness of the stratosphere, however, the temperature must fall below 190$^\circ$ K in order for these water-ice particles to form [55].

Satellite data revealed new information about stratospheric clouds. Observations by the Stratospheric Aerosol Measuring (SAM) II instrument showed that extensive stratospheric clouds exist at temperatures as high as 196$^\circ$ K [29]. These clouds were most likely formed by processes other than sudden cooling.

This recent finding led to the distinction of two important types of PSCs: type I PSCs consist of an aerosol haze of micron-sized nitric acid trihydrate (NAT) crystals, which form at several degrees above the frost point of water; and type II PSCs consist of water crystals which form at lower temperatures of $<190^\circ$ K and are 10 microns in size [57]. Reactions 1.8 and 1.11 have been shown to be enhanced in the presence of NAT as well as ice crystals [1], [17]. Furthermore, another important chemical reaction was shown to be enhanced in the presence of type I PSCs [2]:

$$HOCl + HCl \rightarrow Cl_2 + H_2O$$  \hspace{1cm} (1.12)

It has been theorized that reaction (1.8) occurs via reaction (1.9) followed by Reaction (1.12) [2].

An important product of several of these heterogeneous reactions is $HNO_3$, which
becomes incorporated in the PSC particle itself. Once incorporated into PSCs, $HNO_3$ was found to be efficiently removed from the stratosphere by sedimentation.

In addition to PSCs there are highly concentrated sulfuric acid droplets in the atmosphere [29]. Hanson et al. first reported that reactions between $ClONO_2$, $HCl$ and $N_2O_5$ proceed rapidly on concentrated $H_2SO_4$ solutions [17]. Thus, sulfate aerosols as well as PSCs are believed to be crucial to catalytic ozone depletion.

1.5 Field Data and Unanswered Questions

The first concerted experimental effort to evaluate some of these theories was the National Science Foundation National Ozone Experiment (NOZE I) expedition in the austral spring of 1986. This expedition revealed several important aspects of ozone depletion: (i) ozone was almost completely removed by the beginning of October in the core of the ozone layer; (ii) $OCIO$ column densities were greatly elevated while $NO_2$ levels were low; (iii) $ClO$ densities were elevated; and (iv) chlorine chemistry was, in general, greatly perturbed. Since then, other aircraft campaigns to Antarctica have provided extensive information regarding the chemistry and physics of ozone depletion [3].

Despite the increased knowledge of ozone depletion and its correlation to anthropogenically released halogen compounds, several key questions still remain unanswered. What exactly are the phase and composition of PSCs? How can one accurately describe the heterogeneous reactions that occur on them?

This thesis aims to elucidate the nature of PSCs as well as describe some of the heterogeneous reactions that may occur on them. There are five parts to this thesis. Chapter 2 describes the theory of the liquid-solid phase transition and thus, presents the theoretical background on which a large portion of this thesis is based. Chapter 3 describes the thermodynamics and supercooling characteristics of binary acid solutions relevant to PSCs. Chapter 4 discusses the same issues, but in relation to a ternary acid system. Here, an extensive time study reveals new information about the ternary system. Chapter 5 deals with the theoretical aspects as well as
preliminary experimental data on the vapor pressure of a $H_2SO_4/HCl$ solution and the heterogeneous reaction of $ClONO_2$ on a liquid $H_2SO_4/HCl/H_2O$ film. Finally, the stratospheric implications of the data presented in this thesis are summarized in Chapter 6.
Chapter 2

Theory of Glass Formation

As a solution cools molecular rearrangements lead to the development of a new phase with vastly different thermodynamic and kinetic properties. This solidification occurs either by the formation of a crystalline solid, in which molecules exhibit order on a lattice, or by the formation of an amorphous solid, in which the molecules lack long-range order. While the nucleation process for crystallization is initiated by transient structures brought about through thermal fluctuations, glasses form if the solution is cooled at a sufficiently high rate to prevent nucleation [64].

Glass is generally characterized as a solid with a viscosity greater than $10^{14}$ poises which does not exhibit any long-range order. It was suggested that any liquid will form a glass if the cooling rate is high enough. However, some liquids have a greater tendency towards supercooling and glass formation than others: the larger the kinetic barriers for nucleation and growth, the greater this tendency [15].

The glassy-amorphous solidification of a solution is primarily dependent on the cooling rate or, in other words, the degree of supercooling. In general a liquid will solidify to a glassy state on cooling if the mobility of the molecules has been restricted to prevent their attachment to any nuclei which may be present. This is brought about by the fact that the viscosity of the solution increases considerably upon cooling. Thus, unordered three-dimensional networks may be formed [61].
2.1 Crystallization Behavior of Glasses

The classic work in the specialized field of crystallization behavior of glasses was conducted by G. Tammann. He proposed two factors in determining the behavior of a supercooled solution in terms of glassy or crystalline solidification:

1. The number of crystallization centers (KZ) developing per unit volume per unit time.

2. The linear rate of crystallization growth (KG) of these nuclei in cm/s.

Both factors depend on the degree of supercooling. Tammann’s results in Figure 2-1 show that the curves for both the number of crystal nuclei and the linear rate of growth of these crystals per unit time display pronounced maxima [61].

![Figure 2-1: Dependence of nuclei (KZ) and growth of nuclei (KG) on the supercooling of a glass melt after Vogel [61]](image)

Within a temperature interval below the equilibrium melting temperature of a glass-forming substance there exists a zone in which nuclei do not form at a significant rate but in which crystals, when nucleated, can grow rapidly. Below this temperature...
Zone nuclei may form spontaneously and rapidly. With increased supercooling, both KZ and KG fall to zero as a result of increasing viscosity. This increased viscosity prevents molecules from mobilizing to form nuclei and crystallize.

If the two maxima are small and far apart, i.e. if they occur with different degrees of supercooling, a liquid will easily solidify into a glass. If the maxima occur at the same temperature, then the liquid solidifies to a crystalline and not a glassy solid [61]. Crystallization within the supercooled liquid occurs in the region where the two curves overlap.

When a solution is cooled to the glassy state and then reheated, crystallization almost always occurs during the heating stage. This frequently observed phenomenon can be explained by Tammann’s curves. As a liquid is supercooled to a temperature lower then the temperature at which the number of nuclei (KZ) reaches a maximum, it reaches a zone of supersaturation with respect to number of nuclei. This zone of supersaturation in which both KG and KZ are undetectable occurs as a result of the greater solubility of microscopic embryonic crystallites as compared to macroscopic crystals [28]. Upon warming, the decrease in viscosity allows the necessary mobility to induce spontaneous homogeneous nucleation and thus crystallization occurs. The increasing rate of crystallization rate in a supersaturated glass is responsible for the many instances of crystallization upon warming described in Chapters 3 and 4.

2.2 Nucleation and Crystal Growth

This section briefly describes the homogeneous nucleation and crystal growth of a one-component liquid system. For homogeneous nucleation, the formation of an embryo of a crystalline phase in a surrounding liquid medium is considered. Temperature and external pressure are constant and the embryo will be assumed to be spherical in shape and the crystal-liquid specific surface energy will be assumed isotropic [59].

With these assumptions the free energy of forming a critical nucleus becomes [64]:

\[
\Delta G^* = \frac{16\pi\sigma^3}{3(\Delta G_0)^2}
\]  (2.1)
where $\sigma$ is the crystal-liquid specific surface energy and $\Delta G_v$ is the molecular volume free energy, or the difference between the molecular chemical potential of solid and liquid phases. The number of molecules in a critical nucleus is [59]:

$$n^* = \frac{32\pi}{3V_m} \left( \frac{\sigma}{\Delta G_v} \right)^3$$  \hspace{1cm} (2.2)

where $V_m$ is the molecular volume.

In order to estimate the nucleation rate a steady-state treatment is assumed. In this treatment nuclei are believed to form by a series of bimolecular reactions in which a cluster of a given size grows or shrinks by the gain or loss of a single molecule. The rate at which the number of molecules in an embryo changes is assumed constant. With this assumption the rate of homogeneous nucleation per unit volume is [59]:

$$I_v = K_v \exp \left[ - \frac{\Delta G^* + \Delta G'_m}{kT} \right]$$  \hspace{1cm} (2.3)

where $K_v$ may be taken as:

$$K_v \approx N_v^o \nu_o$$  \hspace{1cm} (2.4)

$\Delta G'_m$ is the energy barrier for diffusion from the bulk solution to the cluster, $\nu_o$ is the number of times per second a molecule attempts this free energy barrier and $N_v^o$ is the number of unassociated molecules per unit time.

Experimental studies of homogeneous nucleation indicate that the lowest temperature to which liquid droplets can be supercooled, $T^*$, lies between $0.75T_E$ and $0.85T_E$, where $T_E$ is the equilibrium temperature (melting point), for nearly all materials. At $T^*$ the free energy of forming the critical nucleus $\Delta G^*$ is typically about $50kT$ [59].
Chapter 3

Binary $H_2SO_4/H_2O$, $HNO_3/H_2O$ and $HCl/H_2O$ Systems

This chapter discusses some of the thermodynamic characteristics of supercooled acid systems. The binary solutions of $H_2SO_4/H_2O$, $HNO_3/H_2O$ and $HCl/H_2O$ were studied using calorimetry. These samples were relatively small. Some binary bulk samples were also analyzed. The purpose of the bulk study was to observe the actual nucleation and crystallization process. Filtering effects, if any, were also determined for the bulk solutions.

The binary solutions studied with calorimetry were conducted in collaboration with Renyi Zhang. The bulk solutions study was conducted in collaboration with Keith Beyer. Refer to the PhD theses of Zhang [70] and Beyer [4] for additional complementary experimental results.

3.1 Sample Preparation

Acid solutions were prepared by diluting concentrated acids with deionized water. The concentrated stock solutions were 96.6 wt % $H_2SO_4$, 70.0 wt % $HNO_3$ and 37 wt % $HCl$. To assess the accuracy of the prepared solutions, the density was measured for each individual solution and compared against known densities as a function of temperature.
3.2 Differential Scanning Calorimeter (DSC)

The binary solutions were analyzed using differential scanning calorimetry. Using the commercial calorimeter Perkin-Elmer DSC-7, transitions between thermodynamically distinct bulk phases were detected and identified. With this, the supercooling characteristics of the binary acid solutions were determined.

Since the solutions analyzed were strong acids, gold-plated or titanium capsules were used. Air, or “dead space” inside these capsules was minimized so as to prevent condensation of liquid onto the cap. These capsules were filled with solution, covered with the appropriate gold-plated or titanium cap, and then sealed with a stainless-steel screw-cap which was tightly placed on the capsule with a volatile sample sealer. Figure 3-1 shows the capsule.

![DSC capsule used in calorimetry experiments](image)

The sample and reference cells were cooled at a constant rate. When the sample underwent a phase transition from liquid to solid, less energy was supplied by the individual heater to the sample cell to maintain it at the same temperature as the
reference cell. In this manner, a liquid to solid transformation manifested itself as a negative peak in the output graph of heat flow vs. temperature. In the case of a heating run, a positive peak emerged to exhibit the solid to liquid transformation. By measuring the area under one of these phase transformation peaks and knowing the mass of the sample, some enthalpies of fusion were determined.

The most frequently used calibrant for the DSC was cyclohexane which has two transition points at -87.06°C and 6.54°C. The coolant was liquid nitrogen and the heating or cooling rate was 4°C/min. Sample sizes varied from 15 to 35 mg. The temperature uncertainty in the DSC was ±0.5°C and uncertainties in enthalpies were less than 10%.

Figure 3-3 shows the cooling and warming runs for pure deionized water: the measured enthalpy of melting was 332.95 J/g, which is less than 0.2% of the literature value of 333.55 J/g [26].

3.3 $H_2SO_4/H_2O$ System

The global sources of sulfur have been well documented in the recent decades. Some quantity of $SO_2$ enters the atmosphere each year from anthropogenic sources, mainly the combustion of fossil fuels and the smelting of metals. Natural sources include vol-
canic emissions of $SO_2$ (and some $H_2S$), generation of particulate sulfate (e.g. in the form of sea salt), and reduced sulfur compounds from the biosphere. The latter class of sulfur compounds include $H_2S, CS_2, COS, CH_3SCH_3, CH_3SH$ and $CH_3S_2CH_3$, with $COS$ being the most prevalent sulfur species. These sulfides are oxidized by $OH$ radicals to $SO_2$ and eventually $H_2SO_4$ if their lifetimes are long enough [65].

The stratospheric background aerosol layer exists at altitudes between 10 and 25 km. It consists mainly of aqueous $H_2SO_4$ particles with an average diameter of $\sim 0.1 \mu m$ and a concentration of $1 - 10 \text{ cm}^{-3}$ [58]. Major volcanic activity, however, may increase the overall sulfur budget by several orders of magnitude, thus increasing the mean concentration of $H_2SO_4$ aerosols. Because stratospheric aerosols are believed to contribute significantly to ozone loss through heterogeneous processes, the study of sulfate aerosols is critical [33], [55], [57]. These background sulfate aerosols may contribute to ozone loss in at least two ways: (i) they may act as nuclei in PSC formation and (ii) they may directly affect active chlorine and $NO_x$ levels by serving
as heterogeneous reaction sites.

At present, the exact role of $H_2SO_4$ aerosols is uncertain. Knowledge concerning the thermodynamic and kinetic nature of the $H_2SO_4$ hydrates is limited. This section investigates the stability of the various hydrates as a function of temperature. In addition, bulk $H_2SO_4$ solutions were analyzed to research the nucleation process and filtering effects on a macroscopic scale.

### 3.3.1 DSC Experiments

Several aqueous $H_2SO_4$ solutions were analyzed to study the solid-solid and liquid-solid transitions for the various hydrates. The solutions ranged from 10 to 73.15 wt % and metastable as well as stable hydrates were identified. The observed hydrates included octa- (SAO), hemihexa- (SAH), tetra- (SAT), tri- (SAR), and dihydrates (SAD)

Heat flow vs temperature graphs of 10.0, 20.0, 35.8, 37.6, 42.4, 47.6, 53.0, 57.7, 64.5 and 73.15 wt % $H_2SO_4$ solutions are presented in Figure 3-4. The 10 and 20 wt % solutions (Figures 2.4a and 2.4b, respectively) exhibit the metastable SAO or stable SAT, and stable SAH as well as ice. Hornung et al. demonstrated that the ice/SAO eutectic exists at -72.4°C while the peritectic between SAO and SAT is at -71.97°C [20]. Because the uncertainty for the DSC is ± .5°C, the difference of .43°C could not be detected. Upon cooling, ice/SAO or ice/SAT formed. The peak near -73°C corresponds to either the solid to solid conversion of SAO to SAH, or the eutectic melting of ice/SAT followed by crystallization into SAH. It is possible that an ice/SAO solution transformed into an ice/SAT solution. If this holds true, the peritectic between SAO and SAT was not detectable by the DSC. Near -62°C, SAH melted at its eutectic with ice and upon further warming, the remaining ice melted at the corresponding equilibrium temperature.

Figure 3-4c shows the phase transitions of a 35.8 wt % solution, which corresponds to the ice/SAH eutectic. Here, the solution did not crystallize upon cooling but rather, upon warming. At -170°C, the solution was a supercooled liquid and at -109°C, the solution crystallized to form the ice/SAO eutectic. This solid underwent a peritectic
transformation to form an ice/SAT solid. This ice/SAT solid then melted to form SAH. The two negative peaks and one positive peak near -72\degree C correspond to these transformations. The ice/SAH eutectic then melted near -61\degree C. The presence of the much smaller peak next to the ice/SAH peak implies that the composition of the solution was slightly greater than 35.8 wt \%. This is because any melt following the ice/SAH melt is due to any remaining solid and does not correspond to the eutectic.

The 37.6 wt \% solution in 3-4d corresponds to the ice/SAT eutectic. Like the 35.8 wt \% mixture the solution supercooled to at least -140\degree C and crystallized upon warming. The peak near -73\degree C indicates a melting of the ice/SAT eutectic. As mentioned previously, it is possible that an ice/SAO was first formed and then transformed to the ice/SAT solid. This transformation could not be detected by the DSC and could not be verified by any other method.

Figure 3-4e shows the cooling and melting of a 42.4 wt \% solution (peritectic between SAH and SAT). Unlike the previous samples neither the ice/SAO nor ice/SAT solid was formed. Instead, the ice/SAH directly crystallized upon warming but instead of melting, it underwent a peritectic reaction near -62\degree C to form the SAH/SAT solid. This peritectic finally melted near -54\degree C.

The 47.6 wt \% solution in Figure 3-4f exhibits several solid phases and transformations. An ice/SAO or ice/SAT eutectic transformed to an ice/SAH near -73\degree C. As with the previous case, it underwent a peritectic reaction to form a SAH/SAT solid. This melted near -54\degree C and the remaining equilibrium solution melted near -40\degree C.

A 53 wt\% solution is shown in Figure 3-4g. This more concentrated solution did not supercool to -140\degree C but crystallized to form the ice/SAO or ice/SAT near -73\degree C. The solid transformed to the ice/SAH eutectic which then peritectically formed a SAH/SAT solid near -54\degree C. The remaining equilibrium solid melted near -32\degree C.

Pure SAT (57.7 wt \%), SAR (52.6 wt \%) and SAD (73.15 wt \%) appear in Figures 3-4h, 3-4i, and 3-4j, respectively. As expected, only one solid was formed for SAT and SAD samples. SAT shows a melt near -26\degree C and SAD melted near -37\degree C. While SAT and SAD crystallized upon warming, SAR never crystallized. Even after several
attempts, SAR remained a supercooled liquid during cooling as well as warming.

The phase transitions presented in Figure 3-4 are in excellent agreement with those in the $H_2SO_4$ phase diagram reported by Gable et al. [13], Mootz and Merschennquack [37], and Hornung et al. [20].

Calorimetric measurements have not been made in great detail in this study. In general, the results correspond closely to those measured by Rubin and Giauque [45], Hornung and Giauque [21], and Hornung et al. [20]. Zeleznik has recently compiled the calorimetric data and compared experimental results to calculations [69]. Figure 3-4h gives a measured heat of fusion of 170.8 J/g for SAT. This is within experimental error of the value of 180.05 J/g obtained by Hornung and Giauque [21] and the value of 169.45 J/g calculated by Zeleznik [69].

![Figure 3-4a: 10 wt% $H_2SO_4$ Solution](image)

Figure 3-4: DSC curves for 10 - 73.15 wt % $H_2SO_4$ solutions. Solid line is cooling curve and dashed line is warming curve.
Figure 3-4 (cont): DSC curves for 10 - 73.15 wt % $H_2SO_4$ solutions

Figure 3-4b: 20 wt % $H_2SO_4$ solution

Figure 3-4c: 35.8 wt % $H_2SO_4$ solution
Figure 3-4 (cont): DSC curves for 10 - 73.15 wt % $H_2SO_4$ solutions

Figure 3-4d: 37.6 wt % $H_2SO_4$ solution

Figure 3-4e: 42.4 wt % $H_2SO_4$ solution
Figure 3-4 (cont): DSC curves for 10 - 73.15 wt % $H_2SO_4$ solutions

Figure 3-4f: 47.6 wt % $H_2SO_4$ solution

Figure 3-4g: 53 wt % $H_2SO_4$ solution
Figure 3-4 (cont): DSC curves for 10 - 73.15 wt % $H_2SO_4$ solutions

Figure 3-4h: 57.7 wt % $H_2SO_4$ solution

Figure 3-4i: 64.5 wt % $H_2SO_4$ solution
Figure 3-4 (cont): DSC curves for 10 - 73.15 wt % $H_2SO_4$ solutions

3.3.2 Glass Transitions

Some information regarding the glass transition of $H_2SO_4$ solutions can be inferred from these calorimetric measurements. Vuillard [63] and Kanno [23] reported glass transition temperatures, $T_g$, for various solutions. They reported an increase in $T_g$ with increasing $H_2SO_4$ concentration. In this study, a similar trend was found. For solutions that did not crystallize while cooling, $T_g$ for dilute solutions was lower than that for more concentrated solutions. The 35.8 and 73.15 wt % solutions entered the glassy state near -127° and -115° C, respectively. $T_g$ for the 42.4 and 47.6 wt % solutions are near -125° C. Upon warming, these glassy solutions returned to the liquid state at the same temperature in which they became glassy solutions, $T_g$. This indicates that the glassy state is characterized by one equilibrium temperature at which both the transition to and from the glass phase occurs.
3.3.3 Supercooling

Hallett and Lewis previously suggested that ice-forming aqueous solutions may supercool just as water supercools [14]. Jensen and Toon predicted a maximum supercooling of 40° C [22]. In this study pure deionized water crystallized near -20° C, as shown in Figure 3-3.

Dilute DSC solutions (10 and 20 wt %) supercooled approximately 20° C, following the prediction made by Hallett and Lewis. As the solutions become more concentrated in \( \text{H}_2\text{SO}_4 \) and thus, less and less like pure water, a large deviation from the predicted value results. Dilute solutions do not supercool readily; ice precipitates out and acts as an efficient nuclei to induce complete crystallization. The 35.8 wt % solution froze near -100° C, close to that predicted by Jensen and Toon [22].

All but the 53 wt % solution supercooled readily to -140° C. These supercooled solutions crystallized only upon warming while the trihydrate solution of 64.5 wt % never crystallized. It is possible that the cooling rate of 4° C/m was too fast. Even if the supercooled solutions were kept at -140° C for an hour, however, the concentrated solutions still did not freeze. As explained earlier, this is because the crystallization rate was extremely low as a result of the increased velocity.

3.3.4 Bulk Solutions

The calorimetric measurements provide some preliminary insight into the supercooling trends of these \( \text{H}_2\text{SO}_4 \) solutions. However, in order to further elucidate the supercooling behavior, filtered and unfiltered bulk samples (20 ml) of compositionally similar \( \text{H}_2\text{SO}_4 \) solutions were analyzed. The experimental apparatus for the bulk study is shown in Figure 3-5 and consisted of a large ethanol bath in contact with a liquid nitrogen reservoir. The temperature of the bath was monitored using a low-temperature thermometer and kept uniform by constantly stirring the bath with a motorized stirrer. The cooling rate of the bath was approximately 0.5° C/m. The filtered samples were drawn through a 0.9 - 1.4 \( \mu \text{m} \) glass frit filter.

The bulk solutions exhibited some expected differences and the results are pre-
Because crystallization is a statistical phenomenon, i.e. a larger volume of solution has a greater probability of crystallizing, these bulk solutions froze at higher temperatures and did not supercool readily. Due to the high viscosity of the solutions at the low temperatures, some of the solutions solidified very slowly after the emergence of crystals. The 35, 37.6, and 40 wt % solutions did not supercool at all. Nuclei formed at or near the equilibrium melting points. The remaining three solutions of 50, 57.6 and 64 wt % solutions supercooled somewhat but not to the extent of the smaller DSC samples described in the previous sections.

In all samples, with the exception of the 40 wt % solution, filtering the samples
decreased the freezing point by 2 to 4°. In the dilute solutions (≤ 40 wt %), filtering drastically reduced the number of visible crystals and as a result, solidification occurred with the noticeable growth and fusion of a few crystals instead of as a gradual hardening of the solution due to an increasing concentration of crystals. In the more concentrated solutions (50 and 57.6 wt %) filtering did not affect the manner of solidification. For both of these solutions, freezing occurred due to a growth of a few or only one crystal. The 64 wt % solution did not solidify at all.

The manner of solidification for the bulk solutions was studied in an attempt to visually classify the different hydrates. The 35 wt % solution became a slush and remained so for a while before it eventually solidified. Most likely the solid slush was an ice precipitate while any remaining liquid solution corresponded to greater than 35 wt % H₂SO₄. This solution nearly solidified near -90° C, approximately 40° below the equilibrium line and consistent with Jensen and Toon [22]. The 37.6 wt % solution corresponds to the ice/SAT eutectic and solidification of this solution occurred as the growth of one solid, the eutectic solution. The 40 wt % solutions yields a coexistence of ice and SAH but the growth of only one solid could be seen. Both the 50 and 57.6 wt % solutions solidified immediately upon the emergence of a few crystals. Only one solid could be distinguished in both solutions - most likely this solid corresponds to SAT.

3.4 \( HNO_3 / H_2O \) system

Similar to ozone, nitric acid undergoes poleward transport and accumulates in the low stratosphere at high latitudes. The absorption spectrum of \( HNO_3 \) reaches beyond 300 nm so that \( HNO_3 \) is somewhat susceptible to photodecomposition in the troposphere and lower stratosphere. At altitudes below 25 km however, \( HNO_3 \) is relatively stable and acts as the major reservoir for \( NO_2 \). A maximum concentration of several ppbv is observed [65].

As mentioned in Sections 1.3 and 1.4, PSCs play a crucial role in the ozone depleting process. Toon et al. suggested that the formation of PSCs involves the
<table>
<thead>
<tr>
<th>$H_2SO_4$ wt %</th>
<th>Crystal- lization</th>
<th>Solidifica- tion</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.0</td>
<td>-59.5° C</td>
<td>to -90.0° C</td>
<td>Many dust-like crystals appeared as the liquid grew viscous. The solution became slushy. Solidification occurred slowly as crystals fused together. At -90° C most of the solution was solid but some viscous liquid remained.</td>
</tr>
<tr>
<td>35.0 F</td>
<td>-66.5° C</td>
<td>-72.5° C</td>
<td>Fewer crystals appeared than in the unfiltered one. A few crystals grew in size to form a solid. The top layer froze first, followed by a downward growth of the solid.</td>
</tr>
<tr>
<td>37.6</td>
<td>-67.0° C</td>
<td>-79.0° C</td>
<td>The crystals were white and square-like in shape. Again, the top layer froze first and the remaining solution followed.</td>
</tr>
<tr>
<td>37.6 F</td>
<td>-69.0° C</td>
<td>-75.5° C</td>
<td>This solution solidified similarly to the 35 wt % filtered solution.</td>
</tr>
<tr>
<td>40.0</td>
<td>-66.0° C</td>
<td>-74.0° C</td>
<td>Numerous crystals grew in size to form one solid.</td>
</tr>
<tr>
<td>40.0 F</td>
<td>-64.5° C</td>
<td>-65.6° C</td>
<td>Only a few crystals emerged. Solidification occurred via the outward growth of these crystals.</td>
</tr>
<tr>
<td>50.0</td>
<td>-58.0° C</td>
<td>-58.0° C</td>
<td>The solution froze rapidly via the outward growth of only one crystal.</td>
</tr>
<tr>
<td>50.0 F</td>
<td>-66.2° C</td>
<td>-66.2° C</td>
<td>Same as above.</td>
</tr>
<tr>
<td>57.6</td>
<td>-68.0° C</td>
<td>-68.0° C</td>
<td>Solidification appeared to have occurred rapidly from one point in the solution since needle-like crystals extended outward from one central point in the solid.</td>
</tr>
<tr>
<td>57.6 F</td>
<td>-70.0° C</td>
<td>-71.0° C</td>
<td>A few crystals fused to form a solid.</td>
</tr>
<tr>
<td>64.0</td>
<td>-71.2° C</td>
<td>to -85.0° C</td>
<td>A few dust-like crystals appeared on the top surface of the solution. The crystals were scattered. At -85° C the remaining liquid was viscous.</td>
</tr>
<tr>
<td>64.0 F</td>
<td>-71.2° C</td>
<td>to -85.0° C</td>
<td>A few localized crystals appeared on the surface but the solution did not harden completely.</td>
</tr>
</tbody>
</table>

Table 3.1: Bulk study. 'F' indicates filtered solutions.
Figure 3-6: $H_2SO_4$ phase diagram with data from this study. Solid line is equilibrium curve from Gable [13]; dashed line is supercooling curve predicted by Hallett and Lewis (supercooling of -21°C) [14]; dotted line is supercooling curve predicted by Jensen and Toon (supercooling of -40°C) [22]; '*' are DSC results; 'O' indicate the crystallization temperature upon cooling of bulk samples; 'X' indicate the final solidification temperature of the bulk samples; '+' indicate the crystallization temperature upon cooling of bulk filtered samples; '+' indicate the final solidification temperature of the bulk filtered samples.
co-condensation of nitric acid and water vapors at temperatures ≤ 200° K below about 25 km in the polar winter stratosphere. They proposed that the type I clouds consist of nitric acid trihydrate, or NAT [54]. Molina et al. and other atmospheric chemists found that ClONO₂ reacts very rapidly with HCl absorbed on ice surfaces, releasing Cl₂. ClONO₂ also reacts with water-ice to form HOCl [35]. Both Cl₂ and HOCl are quickly photolyzed to release atomic chlorine, which can quickly enter the ozone destruction process. Other reactions, such as N₂O₅ + H₂O, also occur readily in the presence of clouds. Later experiments revealed that NAT also catalyzes Cl-activation. Each of these various reactions leads to the removal of active nitrogen and the subsequent production of HNO₃. HNO₃ does not react readily with Cl₂ and remains in the ice. Eventually, the polar stratosphere becomes denoxified and hence, ozone destruction occurs efficiently.

3.4.1 DSC results

Several nitric acid solutions ranging in concentration from 10 - 70 wt % were analyzed with the DSC to identify the various hydrates as well as obtain some thermodynamic data on the binary acid system. The results are presented in Figure 3-7.

Figures 3-7a and 3-7b correspond to the 10 and 20 wt % solutions, respectively. In both cases ice precipitated out first, followed by NAT. The peaks near -43° C indicate a melting of the ice/NAT eutectic. The remaining solids then melted at their equilibrium temperatures of -6° and -16° C. The 32.5 wt % solution consisting of the pure ice/NAT eutectic is presented in Figure 3-7c. Here, the ice and NAT crystallized upon cooling and the pure eutectic melted near -43° C.

The 40 wt % solution is shown in Figure 3-7d. The ice/NAT eutectic froze near -90° C and melted near -43° C. Like the dilute solutions, the remaining solid then melted at its corresponding equilibrium melting point of -30° C. A solution of pure NAT, or 53 wt % HNO₃, crystallized upon cooling near -60° C and melted near -19° C. This is presented in Figure 3-7e. Figure 3-7f shows a 60 wt % solutions. A NAT/NAM (nitric acid monohydrate) eutectic crystallized out first, followed by NAT. The NAT/NAM eutectic melted near -42° C, and the remaining solid melted
near -22° C. The final solution of 70 wt% \( HNO_3 \) in Figure 3-7g is the NAT/NAM eutectic. Like the others, it crystallized upon cooling and melted near -42° C.

The DSC results are in excellent agreement with the experimental results of Kuster and Kremann [25]. The results are summarized in Figure 3-8.

3.4.2 Supercooling

Nitric acid solutions do not supercool readily. It can be seen that for dilute solutions whose concentrations are < 33 wt %, ice precipitates out first, followed by NAT crystallization. Solutions more concentrated than 33 wt % freeze between -60° and -90° C. For a stratospheric temperature of -78° C, most \( HNO_3 \) solutions would be in solid form. In particular, NAT is a solid at this temperature. At temperatures below -90° C, 10 - 70 wt % solutions would be completely frozen.

![Figure 3-7a: 10 wt % \( HNO_3 \) solution](#)

Figure 3-7: DSC curves for 10 - 70 wt % \( HNO_3 \) solutions. Solid line is cooling curve and dashed line is warming curve.
Figure 3-7 (cont): DSC curves for 10 - 70 wt % $HNO_3$ solutions

Figure 3-7b: 20 wt % $HNO_3$ solution

Figure 3-7c: 32.5 wt % $HNO_3$ solution
Figure 3-7 (cont): DSC curves for 10 - 70 wt % $HNO_3$ solutions

Figure 3-7d: 40 wt % $HNO_3$ solution

Figure 3-7e: 53 wt % $HNO_3$ solution
Figure 3-7 (cont): DSC curves for 10 - 70 wt % $HNO_3$ solutions

Figure 3-7f: 60 wt % $HNO_3$ solution

Figure 3-7g: 70 wt % $HNO_3$ solution
Figure 3-8: $HNO_3$ Phase diagram with data from this study. Solid line is equilibrium curve from Kuster and Kremann [25] and '*' are DSC results.
### 3.4.3 Enthalpies of Fusion

Enthalpies of fusion were obtained for various $HNO_3$ solutions. These are presented in Table 3.2. The value of $\Delta H_{fus}$ for NAT of 274.4 J/g is in agreement with the previously reported value of 248.7 J/g by Forsyth and Giauque when considering the range of error for the calorimetric measurements to be 10\% [12].

<table>
<thead>
<tr>
<th>Solid</th>
<th>$T_{melt}$ (in $^\circ$C)</th>
<th>$\Delta H_{fus}$ (in J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NAT</td>
<td>-17</td>
<td>274.4</td>
</tr>
<tr>
<td>ice/NAT</td>
<td>-45</td>
<td>129.3</td>
</tr>
<tr>
<td>NAT/NAM</td>
<td>-43</td>
<td>303.3</td>
</tr>
</tbody>
</table>

Table 3.2: $\Delta H_{fus}$ for various $HNO_3$ hydrates

### 3.5 $HCl/H_2O$ System

$HCl$ behaves similarly to ozone and $HNO_3$ in that it is transported poleward and accumulates in the lower stratosphere. $HCl$ is the main terminal sink for chlorine [65]. Because PSCs can liberate active chlorine from $HCl$, the $HCl/H_2O$ system needs to be well understood. Its role in PSC formation and actual chlorine-releasing mechanism are poorly understood. This section aims to shed light on some of the physical properties of the binary system.

#### 3.5.1 DSC results

DSC data are presented in Figure 3-9. Figure 3-9a shows a 10 wt % solution which froze upon cooling. Most likely, it was ice which precipitated out during the cooling process. Upon warming the ice/hexahydrate (HAH) solid formed and then melted near -74\° C. Following this, the remaining solid melted near -15\° C.

The 23 wt % solution corresponds to the ice/HAH eutectic and is presented in Figure 3-9b. The solution supercooled to -140\° C and froze upon warming. It then melted at its equilibrium temperature of -74\° C. Figure 3-9c shows a 25.2 wt % $HCl$
solution, or pure HAH. It too crystallized while warming and began melting near -73° C. The trihydrate (HAT)/HAH eutectic is shown in Figure 3-9d. This 26.6 wt % solution froze while warming and began to melt at -72° C.

The final HCl solution was composed of 37.6 wt % HCl and is shown in Figure 3-9e. It did not supercool readily. Instead it crystallized near -90° C during cooling and began to melt at -73° C. The HAT/HAH eutectic melted first at this low temperature, followed by the remaining solid near -35° C.

The results from this study are in excellent agreement with those obtained by Vuillard [62], [63] and Pickering [41]. This data is summarized in Figure 3-10.

![Figure 3-9a: 10 wt % HCl solution](image)

Figure 3-9: DSC curve for 10 - 36.6 wt % HCl solutions. Solid line is cooling curve and dashed line is warming curve.
Figure 3-9 (cont): DSC curves for 10 - 36.6 wt % HCl solutions

Figure 3-9b: 23 wt % HCl solution

Figure 3-9c: 25.2 wt % HCl solution
Figure 3-9 (cont): DSC curves for 10 - 36.6 wt % HCl solutions

Figure 3-9d: 26.6 wt % HCl solution

Figure 3-9e: 37.6 wt % HCl solution
### Table 3.3: $\Delta H_{fus}$ for various HCl hydrates

<table>
<thead>
<tr>
<th>Solid</th>
<th>$T_{melt}$ (in °C)</th>
<th>$\Delta H_{fus}$ (in J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAH</td>
<td>-71</td>
<td>193.1</td>
</tr>
<tr>
<td>HAH/HAT</td>
<td>-71</td>
<td>272.4</td>
</tr>
<tr>
<td>ice/HAH</td>
<td>-74</td>
<td>288.3</td>
</tr>
</tbody>
</table>

### 3.5.2 Supercooling

The dilute HCl solution in Figure 3-9a did not supercool readily; ice precipitated out near -30° C while the remaining solution supercooled to -140° C. Upon warming the entire solution froze and melted at the equilibrium temperatures.

The intermediate solutions (23 - 26.6 wt %) supercooled to -140° C each time they were analyzed. They froze only during the warming process and did not appear to have undergone any type of glass transition. The concentrated solution of 37.6 wt % supercooled only to -90° C. Thereafter, it crystallized.

### 3.5.3 Enthalpies of Fusion

Enthalpies of fusion were obtained for the HCl/H$_2$O system and are presented in Table 3.3.
Figure 3-10: HCl phase diagram with data from this study. Solid line is equilibrium line from Vuillard [62], [63] and Pickering [41] and '*' are DSC results.
Chapter 4

Ternary $H_2SO_4/HNO_3/H_2O$ System

Understanding the thermodynamic behavior of the ternary $H_2SO_4/HNO_3/H_2O$ system is crucial for indepth analysis of Cl-catalyzed ozone depletion. The current data on this system is sparse and includes much uncertainty. This section describes experimental results that help elucidate the chemical nature of PSCs and were conducted in collaboration with Beyer [4].

4.1 Time Study

The formation mechanism of type I PSCs remains somewhat unclear. While the existence of $H_2SO_4$ in these particles has been well established, the precise role of sulfate aerosols still remains in question. Experiments which investigated the likelihood that solutions with various compositions and temperatures would freeze were conducted. Consistent with the DSC data in Section 3.3, binary $H_2SO_4/H_2O$ solutions were prone to supercool. When nitric acid was added to these binary $H_2SO_4/H_2O$ solutions, however, freezing occurred often. Thus, the addition of nitric acid was determined to enhance freezing in stratospherically relevant acid solutions.

A stratospheric aerosol composed of concentrated sulfuric acid is in equilibrium with the surrounding molecules. If there is a drop in temperature the vapor pressure of the droplet will decrease and the droplet will begin to absorb water and nitric acid from the atmosphere. This occurs because of the larger amount of $H_2O$ and $HNO_3$
molecules relative to $H_2SO_4$ molecules in the stratosphere. The weight percentage of $H_2SO_4$ in the solution decreases while the $H_2O$ and $HNO_3$ vapor pressures increase. Equilibrium is re-established by a change in the composition of the solution droplet, specifically by a decrease in $H_2SO_4$ and increase in $HNO_3$ and $H_2O$ weight percentages [50].

The gas-liquid equilibrium for the ternary system was predicted by Zhang et al. [71]. They concluded that the $HNO_3$ concentration in liquid stratospheric sulfate aerosols increases rapidly with decreasing temperature. The expected compositions are shown in Figure 4-1 for three sets of stratospheric conditions in which constant $H_2O$ and $HNO_3$ mixing ratios are assumed for each line.

### 4.1.1 Experimental

Preparation of the acid solutions is described in Section 3.1 The ternary solutions analyzed were those predicted by Zhang et al. to have compositions corresponding to polar stratospheric aerosols [71]. These solutions lie on line 'a' on Figure 4-1. To study the effect of $HNO_3$, the freezing characteristic for samples without $HNO_3$, that is, for $H_2SO_4/H_2O$ solutions corresponding to the same water partial pressure and equilibrium temperature as the ternary solutions, were investigated.

The experimental setup is shown in Figure 4-2. 3 ml samples monitored by thermocouples were placed in test tubes immersed in a pre-cooled ethanol bath. This bath was then quickly replaced in the freezer whose temperature was accurately controlled to $\pm 1^\circ$. Freezing was determined by monitoring the rapid rise and fall in temperature which accompanies the liquid-solid phase transition. This data plot of time vs. temperature was acquired by a personal computer.

### 4.1.2 Time Study Results

The length of time required for freezing of samples held at a constant temperature was determined and presented in Table 4-1. Some typical graphs are shown in Figure 4-3.
Figure 4-1: Ternary phase diagram for $H_2SO_4/HNO_3/H_2O$ from Molina et al. [36]. The solid lines are the dilution curves for liquid stratospheric aerosols at 100 mbar ($\sim 16$ km) and at ambient mixing ratios of 5 ppmv $H_2O$ and of (a) 10 ppbv $HNO_3$, (b) 5 ppbv $HNO_3$, and (c) 2.5 ppbv $HNO_3$. Also present in the figure are the equilibrium temperatures (dotted lines), the frost points of crystalline NAT ($S_{NAT} = 1$) ($\bullet$), and the points at which the $HNO_3$ vapor pressure reaches supersaturation of 10 with respect to NAT ($S_{NAT} = 10$) ($\Box$). The ice frost point is 192.6° K for 5 ppmv $H_2O$. The dashed curves are the eutectic lines reported by Carpenter and Lehrman [7]. Also shown is the identity of the various solids that at equilibrium crystallize first upon cooling liquids with compositions bounded by the eutectic lines.
<table>
<thead>
<tr>
<th>$H_2SO_4$ wt %</th>
<th>$HNO_3$ wt %</th>
<th>$T_{eq}$ $^o$ K</th>
<th>$T_{exp}$ $^o$ K</th>
<th># of Samples</th>
<th>* time (hour)</th>
<th>$t_{tot}$ (hour)</th>
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<tr>
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<td>8.9</td>
<td>197.0</td>
<td>188</td>
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<td>27</td>
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<td>8</td>
<td>27</td>
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<td>9</td>
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<td>0.2-15</td>
<td>35</td>
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<td>21.1</td>
<td>24.2</td>
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<td>7</td>
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<td>193.2</td>
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<td>20</td>
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<td>196</td>
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<td>2-4.6</td>
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<td>198</td>
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</tbody>
</table>

Table 4.1: Freezing behavior of supercooled $H_2SO_4/HNO_3/H_2O$ solutions. $T_{eq}$ corresponds to trace 'a' in Figure 4-1, except for the last four entries, which correspond to the $H_2SO_4/H_2O$ system; 48.8 wt % $HNO_3$ corresponds to pure NAT; $T_{exp}$ is the temperature at which the sample was held (fluctuated by ±1$^o$); *time* refers to the time it took to freeze; $t_{tot}$ refers to the total observation time.
Luo et al. calculated homogeneous freezing times of 1 - 100 hours during which 50 % of .1-μm concentrated (47 - 70 wt %) $H_2SO_4$ aerosols would freeze. In particular they predicted a freezing time of 100 hours for 47 - 55 wt % $H_2SO_4$ solutions. These authors pointed out that their calculations are highly sensitive to the assumed values of the diffusion activation energy, which characterizes the homogeneous nucleation process [27]. The results in Table 4.1 for 47.4 and 46.3 wt % solutions show that half or more of the solutions froze within 5.4 hours, suggesting that the diffusion activation energy is most likely larger than the estimate of Luo et al. An additional time study of $H_2SO_4$ was conducted to relate experimental temperature to freezing time and are presented in Table 4.2. The data show that only the solutions of between 45 and 55 wt % freeze readily, even at low temperatures. Other time studies performed on concentrated $H_2SO_4$ solutions by Beyer [5] also suggest the larger activation energy.

Since nucleation is primarily a statistical phenomenon with nucleation probability directly proportional to volume, data in Table 4.1 represent an upper limit to the freezing of compositionally-identical stratospheric aerosols. Zhang et al. demonstrated that ternary solutions with compositions corresponding to those predicted for supercooled sulfate aerosols approaching the ice frost point (for 5 ppmv $H_2O$ at 100 mb, the ice frost point is 192.6° K) freeze readily [71]. Our experimental data is
consistent with this finding. In general, as the equilibrium temperature decreased, and thus the $H_2SO_4$ amount also decreased, the freezing probability of ternary solutions increased. This is especially evident near the equilibrium temperature of $195^\circ$ K where the composition of the ternary solution changes rapidly, as demonstrated by us previously [36] and further described by Beyer [5].

Figure 4-3a: Time study curve of NAT. NAT froze immediately upon placement in the freezer. As a result, no freezing signal is evident.

Figure 4-3: Time study curves. The small oscillations are due to the cycling of the freezer. '*' time' refers to the time it takes to freeze and '*' T' refers to the freezing temperature. The average temperature of the freezer is also indicated along with the uncertainty.
Figure 4-3 (cont): Time study curves.

Figure 4-3b: Time study curve of ternary solution. The peak at 3.57 hours indicates a freezing.

As shown in Figure 4-1 a 1-degree change in equilibrium temperature results in a relatively large change in equilibrium composition, particularly at lower temperatures. Because of the direct relationship between composition and freezing probability, the 1-degree change drastically affects freezing probability. Our data show that while a small ($< 1^\circ$) change in equilibrium temperature (and thus, a significant change in concentration) definitely affects freezing probability, a large change ($\sim 8^\circ$) in the temperature at which the observations are carried out barely perturbs the nucleation probability.

The effect of $\text{HNO}_3$ on the supercooling of stratospheric sulfate aerosols was also studied. This was done by studying freezing probabilities of binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions without $\text{HNO}_3$, but under the same conditions as the ternary solutions. The presence of $\text{HNO}_3$ does not significantly effect supercooling for solutions in which $T_{eq} > 196^\circ$ K. For solutions corresponding to $T_{eq} \leq 196^\circ$ K however, none of the binary $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solutions froze whereas most of the ternary $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{H}_2\text{O}$
Table 4.2: Time study for \( H_2SO_4/H_2O \). \( T_{exp} \) is the temperature at which the sample was held and \(*\) time' indicates freezing time.

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<thead>
<tr>
<th>% ( H_2SO_4 )</th>
<th>( T_{exp} ) (K)</th>
<th>(*) time (h)</th>
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<td>45</td>
<td>193</td>
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<td>70</td>
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</table>

Table 4.2: Time study for \( H_2SO_4/H_2O \). \( T_{exp} \) is the temperature at which the sample was held and \(*\) time’ indicates freezing time.
solutions did. Thus HNO₃ efficiently promotes freezing, particularly for solutions where \( T_{eq} \) is close to the ice frost point. Figures 4-4 and 4-5 summarize the results from the time study.

Figure 4-4 shows clearly the effect of HNO₃ on the solutions. In addition there is a general trend of increasing freezing ratio with decreasing equilibrium temperature. Also seen in this figure is the supercooling trend of H₂SO₄ solutions. The dilute solutions (40.8 - 44.8 wt %) whose concentrations are close to the ice/SAT eutectic rarely froze and most likely formed a glass upon cooling.

Because of the small number of samples and the stochastic nature of crystallization, no information regarding the freezing times of ternary solutions can be inferred from Figure 4-5. However, it is reasonable to theorize that the addition of nitric acid lengthens the time during which the solution is in the liquid phase. Additional experiments are necessary to draw any substantial conclusions in regards to the average freezing time for PSCs.
The stochastic nature of the nucleation process, the limited time scales and number of samples, and the larger sample sizes prevent any definitive information regarding PSCs from being established. These results, however, do provide upper limits to probable freezing temperatures because the presence of a glass surface and larger sample volume can only increase the nucleation rate.

4.2 DSC Results

Some preliminary data regarding the nature of the $H_2SO_4/HNO_3/N_2O$ ternary system was obtained using calorimetric measurements. Several solutions with compositions of 20 - 53 wt % $H_2SO_4$/ 15 wt % $HNO_3$ were analyzed. These ternary solutions will be referred to by their respective $H_2SO_4$ amounts. The results are presented in Figure 4-6.

Figures 4-6a thru 4-6e show DSC curves for these solutions. Only the 20 wt % solution froze and is depicted in Figure 4-6a. Upon cooling, the solution underwent
three phase transitions - two freezings and one glass transition. These most likely represent the freezing of ice followed by the freezing of the NAT/ice eutectic. This is the most probable explanation since $H_2SO_4$ solutions supercool more readily than $HNO_3$ solutions, as discussed in Sections 3.3 and 3.4. The remaining solution supercooled to -140° C whereupon warming, it also froze. By -90° C, the entire solution was solid. The peak near -73° C is similar to the binary $H_2SO_4/H_2O$ solutions in Figure 3-4. In the ternary solution, however, the melting at -73° C is not followed by a crystallization. Thus, this peak most likely represents the melting of the ice/SAT eutectic. Following this the rest of the solution melts near -60° C. This is probably the melting of an ice/NAT/SAT eutectic.

Figure 4-6a: DSC curve for 20 wt % $H_2SO_4/15$ wt % $HNO_3$ solution.

Figure 4-6: DSC curves for ternary solutions. Solid line is cooling curve and dashed line is warming curve.
Figure 4-6 (cont): DSC curves for ternary solutions

Figure 4-6b: DSC curve for 35.8 wt % $\text{H}_2\text{SO}_4$/15 wt % $\text{HNO}_3$ solution.

Figure 4-6c: DSC curve for 37.6 wt % $\text{H}_2\text{SO}_4$/15 wt % $\text{HNO}_3$ solution.
Figure 4-6 (cont): DSC curves for ternary solutions

Figure 4-6d: DSC curve for 42.4 wt % $H_2SO_4/15$ wt % $HNO_3$ solution.

Figure 4-6e: DSC curve for 53 wt % $H_2SO_4/15$ wt % $HNO_3$ solution.
The remaining ternary solutions (35.8, 37.6, 42.4 and 53 wt % \( H_2SO_4 \)) did not freeze at all. Instead they entered a glass phase between -120\(^\circ\) and -110\(^\circ\)C. Like the binary \( H_2SO_4 \) solutions, an increase in \( T_g \) with increasing \( H_2SO_4 \) concentration was found. The 35.8 and 53 wt % solutions entered the glassy state at -120\(^\circ\) and -110\(^\circ\) C, respectively. Addition of the nitric acid enhanced the supercooling of the solutions such that solutions whose concentrations were > 35 wt % remain liquid during both the cooling and warming processes.

In Section 4.1 it was found that the addition of nitric acid to dilute sulfuric acid solutions efficiently induced freezing when the solution was allowed to remain at a constant low temperature for some time. In these DSC studies, however, solutions with concentrations > 35 wt % did not freeze even though nitric acid was present in the solution. In fact, the addition of nitric acid seemed to supercool the solution drastically. There are several possible explanations for this. Perhaps supercooling is highly sensitive to acid composition and only solutions within a certain range of combined \( H_2SO_4/HNO_3/H_2O \) wt % freeze readily. In these DSC samples the addition of 15 wt % \( HNO_3 \) to 35.8 -53 wt % \( H_2SO_4 \) solutions suppressed crystallization whereas in the time study, addition of 13.9 - 24.2 wt % \( HNO_3 \) to 21.2 - 33.2 wt % \( H_2SO_4 \) induced crystallization. It is also possible that the more concentrated the solution is in terms of \( H_2SO_4 \) the more unlikely it is that it will freeze. This general trend is seen in Table 4-1. A more probable explanation is that crystallization occurs much more readily when the solution is allowed to remain at a constant temperature for some length of time. Since the DSC samples were never allowed to remain at the low temperature for any period of time, the samples were unable to establish nuclei and freeze. In addition, it is probable that the heating/cooling rate was too fast. If this is the case the solution became too viscous very quickly, preventing any molecules from mobilizing and inducing crystallization.
Chapter 5

Heterogeneous Chemistry

Recent observations revealed that mid-latitude as well as polar stratospheric chemistry is perturbed. Using both ground-based (Dobson Spectrophotometer) and satellite (Total Ozone Mapping Spectrometer, TOMS, and Stratospheric Aerosol and Gas Experiment, SAGE) instruments, Stolarski et al. showed statistically significant decreases in total ozone. These decreases were observed in all seasons in both the Northern and Southern hemispheres at middle and high latitudes. The declines in total ozone column are as high as 10% per decade [51]. Researchers involved in the Airborne Arctic Stratospheric Experiment (AASE II) discovered thin horizontal layers of ClO with concentrations many times the normal level as equatorward as 22° N. In addition, observed levels of NOx were lower than expected from the Arctic circle to latitudes of the southern United States [40]. The Upper Atmosphere Research Satellite (UARS) mapped ClO abundances from northern Russia to Britain. This large crescent of unusually high ClO levels corresponded to a displaced Arctic vortex and was recorded when the ambient temperature was less than 195° K. This ClO abundance indicates a near-complete conversion of the reservoir forms of Cl (HCl and ClONO2) to the active ozone-depleting form of ClO [66].

A critical question, then, is, what is causing mid-latitude chemistry to be so perturbed? The anomalous levels of ClO and NOx near the equator suggests that there may be other mechanisms aside from PSC chemistry responsible for chlorine activation. One such mechanism may be chlorine activation by the ubiquitous sulfate
Reactions 1.8 thru 1.12 are believed to proceed on sulfate aerosols as well as PSCs. Reaction 1.10

\[ N_2O_5 + H_2O \rightarrow 2HNO_3 \]

has been studied by research groups to have reaction probabilities, \( \gamma \), between .1 and .15 for a range of temperatures and acid concentrations [16], [39]. Reactions 1.8

\[ ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \]

and 1.9

\[ ClONO_2 + H_2O \rightarrow HNO_3 + HOCl \]

were also studied and no significant increase in the uptake of \( ClONO_2 \) was observed on solutions with \( \geq 65 \text{ wt } \% \) \( H_2SO_4 \) and temperatures between 295° and 210° K. The presence of \( HCl \) on these concentrated \( H_2SO_4 \) solutions did not enhance the reaction rate [16], [53]. For more dilute concentrations of \( H_2SO_4 \) much larger reaction probabilities were observed. \( \gamma_{ClONO_2} \) for Reaction 1.9 ranged from .1 to .005 for 40 - 65 wt \% \( H_2SO_4 \) solutions in the temperature range of 200° to 220° K [19].

A strong dependence of \( [HCl]_{aq} \) was observed for dilute \( H_2SO_4 \) (40 - 65 wt \%) solutions in Reaction 1.8. For example, for a 46.6 wt \% \( H_2SO_4 \) solution, \( \gamma = .038, .11 \) and .3 for \( [HCl]_{aq} < 10^{-4}, 10^{-3} \) and \( 6 \times 10^{-3} \), respectively. These results revealed that the reaction \( ClONO_2 + HCl \) on sulfate aerosols may be an important source of active chlorine in the stratosphere and that \( ClONO_2 \) uptake depends on both bulk and surface concentrations of \( HCl \) [19].

Reactions 1.11 and 1.12 have not been studied extensively on liquid \( H_2SO_4 \) films or aerosols. Reaction 1.11 has not been analyzed at all whereas some preliminary data on Reaction 1.12 has been obtained. Again, Reaction 1.12

\[ HOCl + HCl \rightarrow Cl_2 + H_2O \]

was found to depend on \( HCl \) concentration. For a 60 wt \% \( H_2SO_4 \) solution at
220° K, \( \gamma \) for 0.0 and 0.001 wt \% \( HCl \) solutions were \( \sim .01 \) and .1, respectively [31].

Because of the strong dependence of chlorine-activation reactions by sulfate aerosols on \( HCl \), knowing the exact composition of sulfate aerosols is crucial to understanding the possible mechanism responsible for mid-latitude chemistry perturbation. Discrepancies between previously measured vapor pressures of the \( H_2SO_4/HCl/H_2O \) system by Zhang et al. [71] and Hanson and Ravishankara [18] have made it difficult to accurately assess the role of sulfate aerosols in mid-latitude ozone depletion.

This chapter describes an experiment that has been designed to measure vapor pressures and reaction probabilities relevant to stratospheric ozone chemistry. Calibration data and preliminary results are presented so as to ascertain the accuracy of the technique. Successful employment of the wetted-wall flow tube technique described here could shed light on mid-latitude sulfate chemistry.

5.1 Experimental

A schematic of the experimental apparatus is shown in Figure 5-1 and consists of a vertical wetted-wall flow tube coupled to a differentially pumped molecular beam sampling quadrupole mass spectrometer. This technique is similar to that employed by Utter et al. [60] and the molecular beam mass spectrometer (MBMS) system is described by Zhang [70].

5.1.1 Flow Tube

The 2.4 cm i.d. glass flow tube is positioned vertically and consists of two jackets: the inner jacket contains flowing precooled ethanol and the outer jacket is vacuumed for thermal insulation. Attached to the top of the flow tube is the liquid delivery system - an annular cup that overflows to create a falling cylindrical film of acid. This wetted-wall technique has been widely used in the field of chemical engineering and Danckwerts describes the fluid dynamics of such a flow in his classic text [8]. The annular cup has a cooling jacket through which the same coolant from the flow tube flows and is insulated with proper insulation foam. A thermocouple is inserted into
the cup in order to monitor the temperature of the liquid before it falls as a flowing film. There are two inlets on opposite sides of the cup through which the precooled sample enters.

The sample is precooled in the following manner. A reservoir bulb is placed above the flow tube and the flow due to gravity is controlled by a teflon metering valve which allows a volume flow rate of .1 to 1.0 cm$^3$/s. The sample enters the first coiled condenser and is cooled by refrigerated ethanol from a circulating bath. This coolant has a temperature of $\sim -50^\circ$ C. The sample then enters a second coiled condenser which is cooled by the flowing ethanol emerging from the flow tube and annular cup. Since the flow tube and second condenser utilize the same pre-cooled ethanol the temperature of the sample is identical to the temperature of the flow tube when it reaches the sample delivery system. The purpose of the two stage cooling system, which uses two heat exchangers (coiled condensers) with separate coolants, is to minimize heat loss of the flow tube coolant. (The temperature of the coolant is monitored by a thermocouple attached at the return end of the flow.) Without the first condenser, the temperature of the flow tube coolant dropped by as much as 20$^\circ$ C when the sample flowed down the tube for several minutes. With the addition of another condenser this temperature drop was decreased to 4$^\circ$ C.

The liquid collection system consists of a tube leading to a bulb immersed in a dry ice/ethanol bath. The collection reservoir is kept at temperatures below that of the flow tube to ensure a much lower vapor pressure in the collection bulb and thus, to prevent a backflow of vapors that could effect the data. A gas sample from the flow tube is collected by a small tube inserted at the bottom of the flow tube and leading to the MBMS. To prevent liquid from falling into the gas collection tube, a loose teflon guard is placed over it.

Gas reactants are introduced into the flow tube by a movable glass injector (.64 cm o.d.). Since the exposure time of the gas reactant on the falling film can be controlled, a wide range of reaction times is used to deduce heterogeneous reaction rates.
Figure 5-1: Apparatus for wetted-wall flow tube technique. Heat exchangers are coiled condensers and use separate cooling systems.
5.1.2 Molecular Beam Mass Spectrometer

The flow tube can be separated from the MBMS by rotating a small O-ring seal valve with a spring loaded closure mechanism to cover a 1.0 mm pin hole leading to the source ionizer. The MBMS consists of a two stage differentially pumped vacuum system. Gas passing through the pin hole leading to the first stage vacuum chamber, pumped by a 10" diffusion pump, is collimated by a 1.0 mm diameter skimmer cone. The resulting molecular beam enters the second stage vacuum chamber, pumped by a turbomolecular pump, where it is ionized, its signal amplified, and then detected with a lock-in amplifier.

The operating pressure for the first stage of the MBMS system is typically $10^{-6}$ torr while the second stage is near $10^{-7}$ torr. The total pressure in the flow tube is typically .5 - 1 torr so only a small fraction of the main gas is sampled by the MBMS. The remaining gas is removed by a roughing pump.

5.2 Calibration

The stability and linear nature of the mass spectrometer was determined by studying the vapor pressures of 9 molal $HCl$ at various temperatures. A schematic of the calibration system is shown in Figure 5-2.

The successive dilutions of the $He/HCl$ flow results in a partial pressure of $HCl$ determined by

$$ P_{HCl} = \frac{f_1}{f_1 + f_2} \frac{P_{vap}}{P_{sat}} P_{cell} $$

(5.1)

where

- $f_1$ = flow of He thru bubbler (sccm)
- $f_2$ = flow of He as bulk carrier gas (sccm)
- $P_{vap}$ = vapor pressure of 9 molal $HCl$ solution (torr)
- $P_{sat}$ = pressure of bubbler (torr)
- $P_{cell}$ = pressure in flow tube cell (torr)
The system was calibrated by maintaining a constant bulk $He$ flow of $\approx 516$ sccm and a range of bubbler flows from 3 to 48 sccm. The temperature of the solution also varied and ranged from $-40^\circ$ to $-50^\circ$ C. $P_{vap}$ was determined by

$$P_{vap} = T^{3.498} e^{-5750/T}$$  \hspace{1cm} (5.2)$$

where $T$ is in Kelvin.

A typical plot of signal vs. $P_{HCl}$ along with a least-squares fit is presented in Figure 5-3. The mass spectrometer’s detection limit for $HCl$, monitored at mass 36, was $3 \times 10^{-7}$ torr. A calibration was conducted twice a day for several days. Even after a few days had passed, the mass spectrometer displayed relative stability. Thus
Figure 5-3: Calibration curve for 9 molal HCl. '*' are data points and line is least-squares fit.
the mass spectrometer was considered reliable and accurate for a period of several days.

5.3 Preliminary Data

The reaction $\text{ClONO}_2 + \text{HCl} \rightarrow \text{Cl}_2 + \text{HNO}_3$ was qualitatively studied on a flowing film of $\text{H}_2\text{SO}_4/\text{HCl}$. 2 L of a 40 wt % $\text{H}_2\text{SO}_4/\text{HCl}$ solution was prepared by diluting a stock 96 wt % $\text{H}_2\text{SO}_4$ solution. The small amount of $\text{HCl}$ was added using a micropipette.

One major advantage of the wetted-wall technique is that the reaction surface is constantly renewed. While the liquid sample flows along the tube, water evaporates and saturates the carrier gas $\text{He}$. This could effect experimental results by increasing the acid content of the liquid surface. To estimate the change in concentration a mass calculation was performed. The vapor pressure of water over a 40 wt % $\text{H}_2\text{SO}_4$ solution is approximately $10^{-2}$ torr [71]. In order to saturate 2000 cm$^3$/s of $\text{He}$, about $2 \times 10^{-5}$ g of $\text{H}_2\text{O}$ is required per second. Assuming that this is supplied by the top tenth of a millimeter in the first 1 cm of film means that $3 \times 10^{-2}$ g of solution provide $2 \times 10^{-5}$ g to the gas phase. This results in a change of the solution’s concentration by less than 0.1%. A similar analysis for $\text{HCl}$ reveals that a much less significant change in concentration results due to gaseous $\text{HCl}$. Thus, it is unnecessary to provide $\text{H}_2\text{O}$ or $\text{HCl}$ to the carrier or reactant gas streams.

5.3.1 Characterization of the Liquid Flow

Danckwerts describes the fluid dynamics of a liquid film flowing down a cylindrical tube. The thickness of the liquid film is given by

$$\delta = \left(\frac{3\mu V}{\pi gd\rho}\right)^{\frac{1}{3}}$$

(5.3)

where $\mu$ is the viscosity of the liquid (in g/(cm s)), $V$ is the volumetric flow rate (in cm$^3$/s), $g$ is the acceleration due to gravity (980 cm/s$^2$), $d$ is the flow tube diameter.
(2.4 cm) and \( \rho \) is the density of the fluid in g/cm\(^3\) [8]. For the conditions of this experiment, \( \mu \approx 0.5 - 1.5 \), \( V \approx 1 \) and \( \rho \approx 1.5 \) so the liquid film was approximately 0.07 - 1 cm. Because the thickness of the flow depends on the cube root of the volumetric flow rate a change in \( V \) by a factor of 5 changes the thickness of the film by only a factor of 1.6.

The velocity of the fluid at the surface is given by [8]

\[
U_s = \frac{3}{2} \left( \frac{V}{\pi d} \right) \left( \frac{9 \rho}{3 \mu} \right)^{1/3}
\]  

(5.4)

For a volumetric flow rate of 1 cm\(^3\)/s the surface velocity was calculated to be 2.2 - 3.1 cm/s. The observed velocity was \( \approx 2 \) cm/s, close to the calculated value.

To study the turbulence of the flow, the Reynold’s number was calculated from the following equation [8]

\[
Re = \frac{V \rho}{\pi d \mu}
\]  

(5.5)

A turbulent flow is defined as \( Re \geq 500 \) while a laminar flow is given by \( Re \leq 10 \) [60]. For this experiment, \( Re \) was approximately 0.4 - 1, indicating that the flow was laminar.

### 5.3.2 ClONO\(_2\) Uptake

The 40 wt % \( \text{H}_2\text{SO}_4 / .1 \) wt % \( \text{HCl} \) solution was flowed along the cooled tube. The temperature was monitored at 223\(^\circ\) K via a thermocouple placed at the return end of the coolant. \( \text{ClONO}_2 \) was flowed through the movable injector and the injector was pulled up a total of 10 cm in 2 cm increments. The response was monitored at \( m/e = 46 \) for \( \text{NO}_2^+ \). The response is presented in Figure 5-4. As expected the \( \text{ClONO}_2 \) signal decreases exponentially as the exposure time is increased.

The measured first-order loss rate coefficient, \( k_m \), is obtained directly from the plot of signal vs. injector distance. It is defined as

\[
k_m = \frac{d \left( \log S \right)}{dt}
\]  

(5.6)
where $S$ is the mass spectrometer signal. The reaction probability for the wetted-wall flow tube, then, is

$$
\gamma = \frac{2r k_m}{C}
$$

(5.7)

where $r$ is the flow tube radius and $C$ is the thermal velocity of the molecules. $C$ is given by kinetic theory as

$$
C = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}
$$

(5.8)

where $R$ is the gas constant, $T$ is the temperature and $M$ is the molecular weight.

Because of the uncertainty in $[ClONO_2]_{gas}$ for this particular experiment, $k_m$ was not obtained for this preliminary run. The goal of this trial was to demonstrate the feasibility of the experiment by ensuring a proper qualitative signal.

Figure 5-4: MBMS response for $ClONO_2 + HCl$ on sulfuric acid film.
5.3.3 HCl Vapor Pressures

In addition to $\gamma$ measurements $HCl$ vapor pressures can be determined using the wetted-wall technique. In order to ensure accurate absolute measurements the mass spectrometer was calibrated before and after the signals from the flowing liquid were obtained. This wetted-wall technique is convenient because the surface is constantly refreshed, thus eliminating surface depletion. In addition, there are no dilution factors and hence, the margin for error is drastically reduced. The carrier gas becomes saturated with $HCl$ and the signal obtained with the MBMS corresponds directly to $P_{HCl}$.

A vapor pressure measurement for the 40 wt % $H_2SO_4 / .1$ wt % $HCl$ solution was obtained for $T = 226^\circ$ K. The effective Henry’s law coefficient was obtained using

$$H^* = \frac{[HCl]}{P_{HCl}}$$

$HCl$ vapor pressures depend on both the solubility and extent of dissociation:

$$HCl(g) \longrightarrow HCl(aq)$$

$$HCl(aq) \longrightarrow H^+ + Cl^-$$

$$[HCl]_{total} = [HCl(aq)] + [Cl^-] = P_{HCl}H^*$$

Now

$$H^* = H(1 + \frac{K_{5.11}}{[H^+]})$$

where $K_{5.11}$ is the acid dissociation constant.

For an experimental temperature of $226^\circ$ K, $H^* = 1.93 \times 10^6$ M/atm. Zhang reported a value of $1.29 \times 10^6$ [71] and an extrapolated value of $2 \times 10^6$ was obtained from Hanson and Ravishankara [18].
Chapter 6

Conclusion

Evidence for a large upward trend of UV-B radiation has emerged over the past several years. Stamnes et al. reported an increase of UV radiation levels of up to six times the normal values at McMurdo Station during the 1990 ozone hole [49]. UV increases of near 50% were reported in Canada and have been shown to correlate with ozone decreases [24]. With such an increasing threat to the earth’s ecosystem as a result of ozone loss, critical questions concerned with the actual physical mechanism become crucial to solve.

6.1 Implications for Stratospheric Ozone Depletion

The research described in this thesis helps shed light on the PSC formation mechanism. Binary $H_2SO_4/H_2O$ solutions supercool readily; results from this study indicate that stratospheric sulfate aerosols would remain in liquid form unless they encounter temperatures a few degrees below the frost point of ice. If a sufficient amount of $HNO_3$ is added to the solution, however, crystal NAT forms readily. This leads to the formation of PSCs at temperatures several degrees above the ice frost point.

As an air parcel cools and becomes supersaturated with respect to formation of
NAT, the ternary liquid aerosol of $H_2SO_4/HNO_3/H_2O$ becomes supersaturated with respect to crystallization of NAT out of this solution. This follows from our experimental observations that essentially pure NAT crystallizes from ternary solutions [36]. Crystallization of NAT out of liquid aerosol droplets is most likely the first step in the formation of type I PSCs.

Our proposed mechanism of PSC formation is consistent with atmospheric observations that PSCs form when the supersaturation ratio, $S_{NAT}$, with respect to NAT in terms of the $HNO_3$ partial pressure, is at least 10. Our data shows that NAT crystallization occurs readily for compositions and temperatures corresponding to $S_{NAT} \geq 10$. Figure 4-1 shows that the equilibrium composition of the liquid droplets changes drastically as the ice frost point is approached; for a change in temperature from 196.5° to 193.5° K along line 'a', the equilibrium $HNO_3$ concentration changes from 10.4 % to ~ 49 %. As the ice frost point is approached, the equilibrium composition changes very rapidly. Therefore it is likely that stratospheric temperature fluctuations induce crystallization of PSCs, not because of the increase in the degree of supercooling for aerosols of a given concentration but because of the change in equilibrium concentration. With a decrease in $H_2SO_4$ concentration and an increase in $HNO_3$ concentration, the solutions crystallize more readily. The data presented here represent upper limits; nucleation studies with very small particles (micron-sized) are currently in progress and these small particles most likely supercool more readily.

Seeding experiments by us have supported our proposed mechanism of PSC formation. The most commonly suggested mechanism consists of frozen sulfate aerosols providing the nuclei for NAT condensation. In a supercooled solution of NAT, however, SAT crystals were inefficient nuclei for NAT crystallization [36]. Hence, it is unlikely that PSCs are formed by direct condensation of NAT vapor on SAT crystals.

6.2 Future Work

The question of mid-latitude chlorine activation remains unanswered. Using the wetted-wall flow tube technique described in this thesis, several key heterogeneous
reactions will be studied. Reactions 1.8 thru 1.12 are believed to occur on sulfate aerosols under stratospheric conditions but the exact behavior of some of the reactions has not been well established. Currently, Reaction 1.8 on a $\text{H}_2\text{SO}_4/\text{HCl}$ film is being studied to obtain $\gamma$ as well as investigate the threshold equilibrium temperature at which $\gamma$ increases drastically.

Heterogeneous reactions on a quaternary film of $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}$ have not been studied. The reactivity of Reactions 1.8 thru 1.12 can be determined on the quaternary film using the wetted-wall flow tube. This is crucial to understanding stratospheric chemistry since such quaternary aerosols are believed to exist in the stratosphere. Accurate measurements of $\gamma$ on both ternary and quaternary systems using the wetted-wall technique will allow researchers to better understand the role of the ubiquitous sulfate aerosol in ozone depletion as well as better understand the role of the quaternary aerosol.

In addition to $\gamma$ measurements, the wetted-wall technique is currently being used to determine vapor pressures on ternary, and eventually quaternary, systems. The current disagreement on $\text{HCl}$ vapor pressures in the $\text{H}_2\text{SO}_4/\text{HCl}$ system is being investigated. Knowing the precise Henry’s law solubility coefficient will allow researchers to assess the exact composition of sulfate aerosols in terms of $\text{HCl}$ and thus, understand the extent of ozone depletion as a result of heterogeneous sulfate chemistry.

Vapor pressures for the quaternary solution have not been measured. Using this experimental technique the vapor pressures of $\text{HNO}_3$, $\text{HCl}$ and $\text{H}_2\text{O}$ in the $\text{H}_2\text{SO}_4/\text{HNO}_3/\text{HCl}/\text{H}_2\text{O}$ system could be determined. With this, the composition of quaternary aerosol droplets can be known. Studying the heterogeneous reactions that occur on these stratospheric surfaces will further shed light on the mechanism of ozone depletion.
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