Experimental Studies of the Formation
Mechanisms of Type I Polar Stratospheric Clouds

by

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Submitted to the Department of Chemistry
in partial fulfillment of the requirements for the degree of

Doctor of Philosophy
in Chemistry

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

June 1996

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Abstract

The equilibrium chemical composition and physical state of Stratospheric Sulfate Aerosols (SSAs) with enhanced concentration of $HNO_3$ under polar winter conditions (185-220 K) are investigated. Using recently measured vapor pressure data, an alternative numerical approach is proposed for the estimation of SSA composition. Approximated equations which can describe closely the variations of SSA composition with ambient temperature, partial pressures of $HNO_3$ and $H_2O$ are derived. The application of these equations to heterogeneous processing of ozone-rich air inside the polar vortex is then discussed. In the second part of this thesis, the volume density and surface tension of the ternary $H_2SO_4/HNO_3/H_2O$ system are estimated using physico-chemical data of binary systems. Also derived are the vapor pressure equations of micron-sized ternary acid droplets, which include the correction terms for the composition dependence of volume density and surface tension.

Finally, the liquid-solid phase transition of binary $HNO_3/H_2O$ and ternary $H_2SO_4/HNO_3/H_2O$ acid systems are studied using Differential Scanning Calorimetry (DSC). The equilibrium and kinetic phase diagrams of these two systems are constructed using phase transition temperatures of bulk ($\sim 0.3$ to $5 \mu l$) and emulsified ($\sim 20 \mu l$) acid samples, respectively. The average radius of the aqueous droplets in the emulsions is estimated to be $\sim 2.3 \mu m$. The effect of sample cooling rate on the homogeneous nucleation temperature is studied for the range of 0.5 to 100 °C/min. The crystallization kinetics of emulsified acid solutions are analyzed using the crystallization model of Johnson, Mehl and Avrami. Based on these analyses, a plausible mechanism for the transformation of liquid SSAs (Type Ib PSCs) into solid acid hydrates (Type Ia PSCs) is then proposed.

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Acknowledgements

First and foremost, I would like to thank my advisor, Prof. Mario Molina, for his patience, guidance and motivation. Next, I would like to express my deepest gratitude to the other two members of my thesis committee, Prof. Keith Nelson and Prof. Carl Garland. Their precious time and suggestions are appreciated.

The people in the Laboratory of Atmospheric Chemistry, past and present, have been very helpful. They are Matthew Elrod, Rosemary Koch, Danna Leard, Jennifer Lipson, Scott Martin, Roger Meads, Carl Percival, Dara Saledo, John Seeley, Geoff Smith, Darryl Spencer, and Deborah Sykes. The following people deserve special thanks for their assistance and comments in some of my experiments: Keith Beyer, David Dai, Luisa Molina, Huey Ng, Scott Seago, Tun-Li Shen, Paul Wooldridge, and Renyi Zhang.

I am extremely grateful to Sir Edward Youde Memorial Council for providing me a Fellowship. I would also like to thank the MIT Chlorine Project for its generous support of this research in the past few years.

Last, but most important to me, is the recognition of my family’s love and encouragement over the many years I have spent pursuing my education wherever in the world that took me. This thesis is dedicated to them.
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Chapter 1

Introduction

1.1 Background

Concerns about possible depletion of the ozone layer from substances with anthropogenic origins was first raised in the early 1970s, with particular attention paid to the exhaust of Supersonic Transports aircrafts (SSTs) [1, 2, 3]. Flying at an altitude of approximately 20 km, SSTs can inject directly a huge amount of combustion products such as $NO_2$, $SO_2$, $CO_2$, $CO$ and $H_2O$ into the lower stratosphere where very little vertical mixing occurs. The physical lifetimes of these potential ozone-modifying species in the stratosphere are relatively long, ranging from 2 - 4 years; and hence their presence in that region demands some attention. Although the projected fleet of SSTs had not materialized due to some unresolved technical and economical issues, it did successfully direct some scientists’ interests to that part of the atmosphere and eventually led to the discovery of the unexpected detrimental nature of chlorofluorocarbons (CFCs).

The mid-1970s saw the switch of our attention from advanced high-tech aircrafts to the CFC aerosol spray cans. The ozone-depleting potential of CFCs was first proposed by Molina and Rowland [4] who theorized that long-lived CFCs could diffuse up to the lower stratosphere due to the lack of efficient removal processes in the troposphere and reactive chlorine atoms released from the CFCs by photodissociation ($\lambda < 230 \, nm$) would eventually destroy the ozone layer. In a sense, the qualities that make CFCs
commercially useful (viz. transparency, insolubility and inertness) also allow them to survive Nature's cleaning processes in the troposphere.

The catalytic chemistry for loss of odd-oxygen (i.e. $O$ and $O_3$) involving minor constituents have been thoroughly studied, with particular attention paid to the chain reactions involving free radical chlorine oxide $ClO$ [5, 6, 7]:

\begin{align*}
Cl + O_3 & \rightarrow ClO + O_2 \quad (1.1) \\
ClO + O & \rightarrow Cl + O_2 \quad (1.2)
\end{align*}

\[ \text{net: } O_3 + O \rightarrow O_2 + O_2 \quad (1.3) \]

The cycle represented by Reactions (1.1) and (1.2) is so efficient that hundreds of thousands of ozone molecules can be easily destroyed by one single chlorine atom. However, the requirement of a high concentration of atomic oxygen implies that the above cycle only works best in the upper stratosphere where atomic oxygen is abundant. In other words, this catalytic cycle alone cannot explain the massive springtime ozone losses in the lower Antarctic stratosphere, an abnormal phenomenon (commonly known as the Antarctic Ozone Hole) first reported by Farman et al. in 1985 [8].

Solomon et al. [9] and McElroy et al. [10] were among the first to suggest heterogeneous chemistry on the surfaces of Polar Stratospheric Clouds (PSCs) as the key to understand this unusual regional and seasonal loss of ozone. To date, the reactions that are generally considered important are:

\begin{align*}
ClONO_2(g) + HCl(s,l) & \rightarrow Cl(g) + HNO_3(s,l) \quad (1.4) \\
ClONO_2(g) + H_2O(s,l) & \rightarrow HOCl(g) + HNO_3(s,l) \quad (1.5) \\
N_2O_5(g) + HCl(s,l) & \rightarrow ClNO_2(g) + HNO_3(s,l) \quad (1.6) \\
N_2O_5(g) + H_2O(s,l) & \rightarrow 2 HNO_3(s,l) \quad (1.7)
\end{align*}

where the symbols $(s,l)$ and $(g)$ denote solid/liquid phase and gas phase, respectively.
What makes these heterogeneous reactions important is the way they transform stable chlorine reservoir species \((\text{ClONO}_2 \text{ and } \text{HCl})\) into photolabile chlorine compounds \((\text{Cl}_2 \text{ and } \text{HOCl})\) which can be easily converted into the catalytically active form of chlorine (atomic Cl). Together with the \(\text{ClO} - \text{ClO} \) and \(\text{ClO} - \text{BrO} \) dimer reactions proposed respectively by Molina and Molina [11] and McElroy et al. [12], the sudden appearance of the \textit{Antarctic Ozone Hole} in the mid-1980s can be satisfactorily explained [10].

Three types of PSCs have been frequently observed in the stratosphere. Type Ia, the most commonly sighted PSCs (temperature \(\sim 195 \text{ K}\)), is composed mostly of nitric acid and water. Early theoretical and field studies [13, 14, 15, 16] pointed to nitric acid trihydrate (NAT) as its most likely form. Recent field measurements [17, 18, 19, 20, 21, 22] and laboratory studies [23, 24, 25] have provided concrete evidence for the existence of another kind of cloud particles which can also form above the frost point of ice and have the physical characteristics of supercooled liquid aerosols. Under certain conditions, this kind of metastable liquid particles, generally known as Type Ib PSCs, can be as abundant as Type Ia PSCs. The background stratospheric sulfate aerosols (SSAs) are thought to be the precursors for the formation of both Ia and Ib PSC particles through the condensation of \(\text{HNO}_3\) and \(\text{H}_2\text{O}\) vapor molecules. Unfortunately, the actual microphysical processes involved during the phase transformation are far too complicated to be understood with our present knowledge. Type II PSCs are essentially ice particles with diameters in the range of several microns formed by water vapor condensation on Type Ia or Ib PSCs at temperature lower than or equal to the ice frost point.

Besides PSCs, background stratospheric sulfate aerosols (SSAs) represent another main category of heterogeneous particles in the lower stratosphere. The existence of a permanent layer of sulfuric acid aerosols in the stratosphere has been known for several decades. It was Junge [26] who first attempted to study the physical state and chemical composition of this aerosol layer. SSAs are especially important in providing an explanation for ozone depletion in the mid-latitude where the temperature seldom goes below \(210 \text{ K}\). The chemical composition of background SSAs is controlled by
several simultaneous atmospheric processes such as production at the sources, trans-
port and mixing of air masses, chemical and physical transformation, and the removal 
processes of dry deposition and precipitation scavenging.

The issue of utmost significance is to understand under what conditions will the 
sporadic Arctic Ozone Hole appear. Also important are the size and depth of this 
ozone hole. To answer these questions, one has to realize that the average winter time 
temperature in the Arctic is not as low as that in the Antarctic and very often the 
lowest temperature in the Arctic may still be slightly higher than the frost point of 
ice. In other words, most of the stratospheric clouds sighted in the Arctic are Type 
I PSCs and hence the relative amount of Type Ia and Ib PSCs may be important in 
understanding the extent of ozone depletion inside the Arctic vortex.

Studies in the past have shown that phase transformation processes of the SSAs 
assume several important roles in the lower stratosphere. First of all, the gas-liquid 
transformation can provide efficient pseudo sinks for condensible trace gases such as 
\( HNO_3 \), \( HCl \) and \( HBr \). The liquid-solid transformation, as just mentioned above, 
controls the extent of heterogeneous chemical processing in the lower polar strato-
sphere. Finally, both gas-liquid and liquid-solid transformations are expected to influence 
directly the annual radiation budget of the Earth due to the different scattering 
properties of solid and liquid aerosols.

In the so-called 3-stage PSC formation mechanism, the background sulfate aerosol 
particles (presumed to be frozen) are assumed to serve as nuclei for the condensation 
of nitric acid and water vapor during the formation of Type Ia PSCs. The actual 
mechanism involved, however, is still under investigation. The equilibrium phase 
diagrams of multi-component systems can provide valuable information about the 
phase transformation behavior. In many cases, the construction of such a diagram 
may be accomplished by means of Differential Scanning Calorimetry (DSC) [27, 28, 
29]. Some of the DSC experiments reported in this study have been performed on 
emulsion samples which are usually considered to provide a means of avoiding, at 
least for the most part, heterogeneous nucleation.

It is the main purpose of this study to obtain useful experimental liquid-to-solid
transition data for the construction of plausible formation mechanisms for the two subclasses of Type I PSCs. Together with the results from previously published studies, it is hoped that one can eventually predict the extent of heterogeneous processing inside the polar vortices using laboratory and field measurement data, and hence the dimensions and duration of the annual *Polar Ozone Holes*.

1.2 Thesis Outlines

The vapor pressures, condensation temperature and composition of supercooled nitric acid solutions are reviewed in the first part of chapter 2. Using recently measured vapor pressures of ternary $H_2SO_4/HNO_3/H_2O$ solutions, the composition of SSAs under typical polar stratospheric conditions is then estimated numerically. Approximated equations which can describe closely the variations of SSA composition with temperature and partial pressures of $HNO_3$ and $H_2O$ down to the condensation temperature of nitric acid are derived. The implications of these equations for stratospheric heterogeneous chemistry are then discussed.

In Chapter 3, three of the most important physico-chemical parameters in the study of microphysical processes of ternary acid aerosols, viz. Kelvin equations for multi-component systems, density and surface tension, are estimated.

The last part of this thesis (Chapter 4) is devoted to the experimental studies of liquid-solid and solid-solid phase transitions of binary $HNO_3/H_2O$ and ternary $H_2SO_4/HNO_3/H_2O$ systems using Differential Scanning Calorimetry (DSC). Acid emulsions are developed for the measurements of homogeneous freezing temperatures. Equilibrium and kinetic phase diagrams of both bulk and emulsified acid systems are constructed and plausible formation mechanisms for Type Ia and Ib PSCs are proposed. Finally, the crystallization kinetics of the emulsified acid systems are analyzed using the Johnson-Mehl-Avrami (JMA) model of phase transformations.
Chapter 2

Equilibrium Composition of Stratospheric Sulfate Aerosols

2.1 Introduction

The chemical composition and physical state of stratospheric sulfate aerosols\(^1\) (SSAs) have been the focus of atmospheric research ever since their discovery in 1961 by Junge et al [30]. It is generally agreed that SSAs exist in the form of highly dispersed mist of supercooled sulfuric acid droplets, which can be found mostly between the tropopause and 30 km in the middle stratosphere. Field measurements in the last decade have clearly shown that this thin layer of acid aerosols is chemically persistent and globally distributed.

Experimental and theoretical knowledge of this sulfate aerosol layer (also known as the *Junge layer*) has increased rapidly in the past few years, in part due to the recent advancement in both direct and remote sensing techniques. After the unexpected discovery of the *Antarctic Ozone Hole* phenomenon, research on the Junge layer has also been spurred by the realization that SSA particles, like PSCs, can also promote the chemical transformation of the relatively inert chlorine reservoir compounds such

\(^1\)The term "stratospheric sulfate aerosols" and the acronym "SSAs" are loosely used in the following studies to represent both background sulfate aerosols \(T > \sim 195 \, K\) and Type Ib PSCs \(\sim 195 \, K > T > \text{ice frost point}\).
as $HCl$ and $ClONO_2$ to the more photolabile forms (e.g. $Cl_2$ and $HOCl$) [31, 32]. The latter form of chlorine species has been shown by both laboratory experiments [33] and field measurements [34] to be the principal source of active chlorine radicals in the lower stratosphere.

As mentioned in Chapter one, one of the outstanding issues in the study of ozone depletion is the unmistakable downward trend of column ozone level in the middle latitudes. Recently this trend has been shown to be both statistically significant and persistent [35]. Large scale computer simulation [36, 37] have demonstrated that this observed trend can be reproduced in the simulation if the chemical processing potential of SSAs is also included in the model. Preliminary laboratory measurements [38, 36, 39] also support this point although more refined experiments are needed to draw the final conclusion.

In this chapter, the equilibrium compositions of SSAs are estimated by solving the ternary acid vapor pressure equations of Beyer et al. [40] both numerically and analytically. Reasonable approximations are made to simplify the vapor pressure equations. As a background introduction, the supercooled $HNO_3/H_2O$ binary acid system is briefly reviewed before the analysis. The importance of this analysis in understanding the formation of PSCs and their role in the depletion of polar ozone will be discussed at the end of this chapter.

### 2.2 Supercooled $HNO_3/H_2O$ Solution Droplets

The abundance of nitrogen-containing species in the atmosphere has been one of main issues in the field of atmospheric chemistry. Among those species of special interest are $NO_x^2$, $N_2O_5$, $HNO_4$, $ClONO_2$, $PAN^3$ and $HNO_3$. Knowledge of the spatial and temporal distribution of $NO_y^4$ is critical for the accurate estimation of

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2 The use of $NO_x$ here refers to $NO$ and $NO_2$.

3 $PAN$ stands for Peroxyacetyl Nitrate.

4 In the lower stratosphere, the total reactive odd nitrogen, $NO_y$ is defined as

$$NO_y = NO + NO_3 + HNO_2 + HNO_3 + 2(N_2O_5) + HO_2NO_2 + ClONO_2 + BrONO_2 + CH_3C(O)OONO_2 + aerosol nitrate + \ldots$$
the composition of SSAs, especially at temperatures low enough for an appreciable amount of trace species such as \( \text{HNO}_3 \) to condense. Recent laboratory measurements by Zhang et al. \([41, 23]\) have shown that the composition of ternary liquid stratospheric aerosols changes rapidly as the temperature approaches the condensation point of nitric acid solution. In fact, supercooled binary nitric acid solution can be used to represent the lower temperature limit of the “deliquescence”\(^5\) curve of SSAs. In this section, the condensation points of supercooled nitric acid solutions under a variety of conditions are estimated using recently measured vapor pressure data \([14, 13]\).

The formation and destruction of nitric acid molecules in the lower stratosphere by the three-body processes

\[
\begin{align*}
\text{HO} + \text{NO}_2 + M &\rightarrow \text{HONO}_2 + M \quad (2.1) \\
\text{HO}_2 + \text{NO} + M &\rightarrow \text{HONO}_2 + M \quad (2.2)
\end{align*}
\]

and the photolysis of \( \text{HNO}_3 \)

\[
\text{HNO}_3 + h\nu (\lambda \leq 330nm) \rightarrow \text{OH} + \text{NO}_2 \quad (2.3)
\]

represents one of the most important holding cycles of nitrogen involving species from both the \( \text{HO}_x \) and \( \text{NO}_x \) families. As the photolysis process is relatively slow comparing with the three-body reactions at lower stratosphere, it is estimated that nearly half of the stratospheric load of \( \text{NO}_x \) appears in the form of \( \text{HNO}_3 \) molecules. The significance of this piece of information lies on the fact that nitric acid is substantially more soluble in aqueous systems such as rain droplets than other \( \text{NO}_y \) species. That means a constant flux of nitrogen species from the stratosphere to the troposphere could be established through atmospheric scavenging processes such as rain-out. It should be pointed out that the denitrification process just described is slightly different from a similar process due to the sedimentation of large PSC particles.

\(^5\) The term \textit{deliquescence} has been used here to describe the condensation of both \( \text{H}_2\text{O} \) and \( \text{HNO}_3 \) vapor molecules from the ambient atmosphere to the SSAs.

\(^6\) For practical purposes, the approximation \( \text{NO}_y \approx \text{NO}_x + \text{HNO}_3 \) is usually made.
There is clear evidence that $HNO_3$ plays an important role in the formation of Type I PSCs. Early theoretical studies focused on extrapolating room temperature nitric acid vapor pressure data [42] to temperatures found in the winter polar stratosphere [43, 10, 44]. Recently, Hanson and Mauersberger [13] and Hanson[14] have studied this system at temperatures that are close to those at the lower stratosphere. They measured the vapor pressure of supercooled nitric acid solutions of mole fraction ranging from 0.2 to 0.4 at 263.2, 243.9 and 222.2K. The results they obtained further support the general viewpoint that aerosol particles (liquid or solid) containing mostly $HNO_3$ and $H_2O$ could exist in the winter polar stratosphere.

One of the many difficulties encountered by Hanson and Mauersberger in their experiments involves supercooling the nitric acid solutions to temperatures of stratospheric interest. Unlike concentrated sulfuric acid, bulk solutions of nitric acid are known to form crystal hydrates almost instantaneously when the appropriate temperature (usually close to the equilibrium melting temperature of the hydrates) is reached. Therefore, Hanson [14] obtained most of the lower temperature vapor pressure values by extrapolating the higher temperature data. The uncertainty they estimated for their condensation temperatures is about ±0.8K, or ±1K if the possible systematic variation of the partial molal latent heats is also considered. It should be emphasized at this point that even though bulk supercooled solution of nitric acid under typical stratospheric conditions is highly unstable comparing with its hydrate forms such as NAT and NAD, it is still conceivable for us to find supercooled microdroplets composed mainly of nitric acid and water in the stratosphere. The size effect on the degree of supercooling will be further discussed in Chapter 4. In the remains of this section, recent experimental vapor pressure data of the $HNO_3/H_2O$ binary system are re-analyzed and expressed in a form that will be useful for later studies.

For a n-component system at constant temperature and pressure, an approximate form of the Gibbs-Duhem equation can be written as

$$\sum_{i=1}^{n} X_i d\ln P_i \approx 0$$  \hspace{1cm} (2.4)
Table 2.1: Coefficients for Eqs. (2.7) and (2.8)

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$d$</th>
<th>$e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>-2.398</td>
<td>-6.746</td>
<td>-1.638</td>
<td>8.394</td>
<td>8.646</td>
</tr>
<tr>
<td>$B_i$</td>
<td>-4071</td>
<td>2402</td>
<td>-1084</td>
<td>1321</td>
<td>2173</td>
</tr>
</tbody>
</table>

where $X_i$ is the mole fraction of species $i$ in the condensed phase and $P_i$ the corresponding partial vapor pressure for that species. For the $HNO_3/H_2O$ binary system Eq. (2.4) becomes

$$X \, d \ln P_{HNO_3} + (1 - X) \, d \ln P_{H_2O} = 0$$

(2.5)

where $X$ is the mole fraction of nitric acid. The above equation can also be written in a more practical form, known as the *Duhem-Margules equation*

$$X \left( \frac{\partial \ln P_{HNO_3}}{\partial X} \right)_T = (X - 1) \left( \frac{\partial \ln P_{H_2O}}{\partial X} \right)_T$$

(2.6)

which shows explicitly the relationship between the gradients of the vapor pressure-composition curves of $HNO_3$ and $H_2O$. For binary system over a limited composition range, equations of the form

$$\log P_{HNO_3} = aX^2 + bX + c\ln(X) + d$$

(2.7)

$$\log P_{H_2O} = aX^2 + (2a + b)X + (2a + b + c)\ln(1 - X) + e$$

(2.8)

are commonly used for the fitting of experimental data[42]. Here, the coefficients assume the simple temperature dependent form of $i = A_i/B_i/T$ (see Table 2.1 for the values of coefficients $A_i$ and $B_i$). Note that Eq. (2.8) can be easily derived by applying the *Duhem-Margules relationship* to Eq. (2.7). In the lower stratosphere, the ambient partial pressures of $HNO_3$ and $H_2O$ are usually quite constant at temperatures above the nitric acid condensation temperature (also known as the nitric acid *dew point*, $T_d$). This condensation point can be easily determined by solving simultaneously
Eqs. (2.7) and (2.8):

\[ T_d = \frac{B_{HNO_3}}{A_{HNO_3} - \log P_{HNO_3}} = \frac{B_{H_2O}}{A_{H_2O} - \log P_{H_2O}} \]  

(2.9)

where

\[ A_{HNO_3} = A_a X_d^2 + A_b X_d + A_c \ln X_d + A_d \]
\[ B_{HNO_3} = B_a X_d^2 + B_b X_d + B_c \ln X_d + B_d \]
\[ A_{H_2O} = A_a X_d^2 + (2A_a + A_b) X_d + (2A_a + A_b + A_c) \ln(1 - X_d) + A_e \]
\[ B_{H_2O} = B_a X_d^2 + (2B_a + B_b) X_d + (2B_a + B_b + B_c) \ln(1 - X_d) + B_e \]

In the above equations, \( X_d \) is the mole fraction of nitric acid at the *dew point*. It can be calculated by solving Eq. (2.9) recursively. The weight fraction \( x \) of \( HNO_3 \) is simply related to the mole fraction \( X \) as follows,

\[ x = \frac{1}{1 + \frac{M_{H_2O}}{M_{HNO_3}} \left( \frac{1}{X} - 1 \right)} \]  

(2.10)

where \( M_{H_2O} \) and \( M_{HNO_3} \) are the molecular weight of water and nitric acid respectively.

In this study, weight fraction is chosen as the scale for acid composition.

At the nitric acid condensation point, the number of components and phases of the \( HNO_3/H_2O \) binary system are both two and so according to the Gibbs phase rule\(^6\), there are only two degrees of freedom. In other words, both the condensation temperature and nitric acid weight fraction are dependent variables with values controlled by the ambient partial pressure of \( HNO_3 \) and \( H_2O \). Figure 2-1 is a plot of \( HNO_3/H_2O \) condensation temperature against the ambient partial pressure of nitric acid under typical conditions of lower stratosphere (16 km, \( \sim 100 \) mbar). The

\(^6\)Gibbs phase rule for bulk phases:

\[ F = C - P + 2 \]

where \( F \), \( C \) and \( P \) are the number of degrees of freedom, components and phases respectively.
Figure 2-1: Dependence of $HNO_3/H_2O$ condensation temperature on the partial pressure of $HNO_3$ in the stratosphere at 16km ($\sim 100mbar$). The lines represent the power law fit of the calculated points (refer to Eq. (2.11) and Table 2.2).
Figure 2-2: Dependence of \( HNO_3/H_2O \) condensation temperature on the partial pressure of \( H_2O \) in the stratosphere at 16 km (~100 mbar). The lines represent the power law fit of the calculated points (refer to Eq. (2.11) and Table 2.2).
ambient water vapor partial pressure varies from 1 ppmv to 10 ppmv and the dew points of pure water (i.e. \( P_{HNO_3} = 0 \)) are calculated using Eq. (2.16). It is obvious from the figure that within this range of \( H_2O \) partial pressure, a change of \( P_{HNO_3} \) from 1 ppbv to 10 ppbv will only increase the \( HNO_3/H_2O \) condensation temperature by approximately 3K. On the other hand, the condensation temperature goes up almost 11K when \( P_{H_2O} \) increases from 1 ppmv to 10 ppmv under a constant \( P_{HNO_3} \). This point is clearly illustrated in Figure 2-2 in which the partial pressure of \( H_2O \) is used as the variable instead.

Another important feature of the plots is the highly nonlinear relationship between the condensation temperature and the partial pressure of \( HNO_3 \) and \( H_2O \). It has been found that a simple power law of the form

\[
T_d = \alpha_i^T P_i^{\beta_i^T} + \gamma_i^T
\]

(2.11)

can be used to describe satisfactorily this relationship. The fitted coefficients \( \alpha_i^T, \beta_i^T \) and \( \gamma_i^T \) for both \( HNO_3 \) and \( H_2O \) are tabulated in Table 2.2. Judging from the data

<table>
<thead>
<tr>
<th>( P_{H_2O} ) or ( P_{HNO_3} )</th>
<th>( ppmv ) (( H_2O )) or ( ppbv ) (( HNO_3 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>( \alpha_{HNO_3}^T )</td>
<td>4.1313</td>
</tr>
<tr>
<td>( \beta_{HNO_3}^T )</td>
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</tr>
<tr>
<td>( \gamma_{HNO_3}^T )</td>
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</tr>
<tr>
<td>( \alpha_{H_2O}^T )</td>
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<tr>
<td>( \beta_{H_2O}^T )</td>
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</tr>
<tr>
<td>( \gamma_{H_2O}^T )</td>
<td>0</td>
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<tr>
<td>( \alpha_{HNO_3}^T )</td>
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<tr>
<td>( \beta_{HNO_3}^T )</td>
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<td>( \gamma_{HNO_3}^T )</td>
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</tr>
<tr>
<td>( \alpha_{H_2O}^T )</td>
<td>185.38</td>
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<tr>
<td>( \beta_{H_2O}^T )</td>
<td>0.024367</td>
</tr>
<tr>
<td>( \gamma_{H_2O}^T )</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 2.2: Coefficients \( \alpha_i^T, \beta_i^T \) and \( \gamma_i^T \) for Eq. (2.11). The ranges of \( P_{HNO_3} \) and \( P_{H_2O} \) are the same as in Figure 2-1.
Table 2.3: Coefficients $\alpha_i^x$, $\beta_i^x$ and $\gamma_i^x$ for Eq. (2.12). The ranges of $P_{HNO_3}$ and $P_{H_2O}$ are the same as in Figure 2-3.

shown in Figure 2-1 and 2-2, we conclude that $T_d$ is more susceptible to the relative changes in $P_{H_2O}$ than in $P_{HNO_3}$.

Unlike $T_d$, the weight percentage of $HNO_3$ at the dew point ($x_d$) actually decreases with increasing $P_{H_2O}$. This is consistent with our intuition that the higher the ambient vapor concentration of $H_2O$, the higher the water content of the condensate. The dew point weight percentage of nitric acid is plotted against $P_{HNO_3}$ and $P_{H_2O}$ in Figures 2-3 and 2-4 respectively. The same stratospheric conditions of Figure 2-1 and 2-2 are used for the calculation. Once again, the calculated $x_d$’s are fitted to a power law of the form

$$x_d = \alpha_i^x P_i^{\beta_i^x} + \gamma_i^x$$

(2.12)

for the sake of convenience. In order to make sure that the fitted curves would approach the correct boundary conditions, theoretical points $x_d = 0$ wt% (as $P_{HNO_3} \to 0$) and $x_d = 100$ wt% (as $P_{H_2O} \to 0$) were added to Figure 2-3 and 2-4 respectively before the fitting. The fitted coefficients $\alpha_i^x$, $\beta_i^x$ and $\gamma_i^x$ are listed in Table 2.3. As illustrated in the two figures, $x_d$ varies from 40 wt% to 58 wt% for the conditions
Figure 2-3: Dependence of weight percentage of $HNO_3$ on the partial pressure of $HNO_3$ in the stratosphere at 16 km ($\sim 100mbar$). The lines represent the power law fit of the calculated points (refer to Eq. (2.12) and Table 2.3).
Figure 2-4: Dependence of weight percentage of $HNO_3$ on the partial pressure of $H_2O$ in the stratosphere at 16 km ($\sim 100 mbar$). The lines represent the power law fit of the calculated points (see Eq. (2.12) and Table 2.3).
considered here. Again the value of $x_d$ appears to be more susceptible to changes in $P_{H_2O}$ than to changes in $P_{HNO_3}$, although not by much.

### 2.3 Sulfate/Nitrate Aerosol Model

The possibility that stratospheric aerosols are composed of more than one major mineral acid was proposed in 1974 by Kiang and Hamill[45]. In their analysis, room temperature vapor pressure data were extrapolated to temperatures of stratospheric interest. By simply comparing the estimated vapor pressures of $H_2SO_4/HNO_3/H_2O$ ternary acid solution with the measured partial pressures of water and nitric acid in the stratosphere, they concluded that nitric acid might participate in the formation process of SSAs. According to their crude calculation, the aerosol particles would have a composition of approximately 75 % by weight of $H_2SO_4$ and 10 % by weight of $HNO_3$ at -50°C under typical stratospheric conditions ($P_{HNO_3} : 10^{-7} - 10^{-6}$ torr, $P_{H_2O} : 10^{-4} - 10^{-3}$ torr).

Theoretical calculations have also been performed by Jaecker-Voirol et al.[46] for the vapor pressures of ternary system $H_2SO_4/HNO_3/H_2O$ and the two binary systems $H_2SO_4/H_2O$ and $HNO_3/H_2O$. They developed a set of Van Laar type equations based on the method of Li and Coull [47]. They then applied the theoretical equations to data measured by Vandoni[48] and concluded that the direct formation of ternary aerosols as predicted by Kiang et al. was highly improbable. Nonetheless, their argument was based on a wrong premise. In their analysis, they used the same assumption of Kiang and Hamill such that the condensed phase (i.e. the suspending aerosol micro-droplets) is of sufficient size to alter the ambient partial pressure of $HNO_3$ and $H_2O$ in the stratosphere. Consequently, at a particular temperature, the existence of a minimum in the total droplet vapor pressure becomes a necessary condition for stable ternary acid aerosols. This assumption is, of course, not valid in the lower stratosphere as field measurements in the past few years have already demonstrated the constancy of vapor concentrations of $HNO_3$ and $H_2O$ in that part of the atmosphere during the initial cooling period of polar winter. Significant deple-
tion was only observed when the stratospheric temperature was close to the freezing point of water. At such low temperature, it is anticipated that a considerable fraction of the supercooled aerosol particles will grow to size of a few microns.

### 2.3.1 Vapor Pressure of $H_2SO_4/HNO_3/H_2O$ System

Using the vapor pressure data of Zhang et al. [41, 49], Beyer [50] proposed the following equations for the $H_2SO_4/HNO_3/H_2O$ ternary system:

\[
\log P_{HNO_3} = \log x + \log P^0_{HNO_3} + a_0 + a_1(1 - x - y) - a_2 \exp(1 - y)^8 - 1 \tag{2.13}
\]

\[
\log P_{H_2O} = \log(1 - x - y) + \log P^0_{H_2O} + b_0 + b_1(x + y) + b_2(x + y)^2 - b_3 \exp(1 - y)^8 - 1 \tag{2.14}
\]

where $x$ and $y$ are the weight fraction of $HNO_3$ and $H_2SO_4$ respectively. The difference between Zhang’s original equations and the above new parameterization is that the latter is based on the Raoult’s law for non-ideal solutions. Similar to Eqs. (2.7) and (2.8), the coefficients $a_i$ and $b_i$ are expressed in the form of $A_i - B_i/T$ and are tabulated in Table 2.4. The vapor pressure of pure nitric acid and water (in torr) are given as [51, 52]:

\[
\log P^0_{HNO_3} = 7.61628 - \frac{1486.238}{T - 43} \tag{2.15}
\]

\[
\log P^0_{H_2O} = 8.30436 - \frac{1827.18}{T} - \frac{71208.3}{T^2} \tag{2.16}
\]

Eq. (2.13) and (2.14) can be further simplified by incorporating the pure vapor

<table>
<thead>
<tr>
<th></th>
<th>$a_0$</th>
<th>$a_1$</th>
<th>$a_2$</th>
<th>$b_0$</th>
<th>$b_1$</th>
<th>$b_2$</th>
<th>$b_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_i$</td>
<td>2.648</td>
<td>-4.465</td>
<td>-0.569</td>
<td>1.991</td>
<td>-10.17</td>
<td>10.55</td>
<td>0.1187</td>
</tr>
<tr>
<td>$B_i$</td>
<td>314.7</td>
<td>685.5</td>
<td>-189.9</td>
<td>659.8</td>
<td>-3466</td>
<td>4224</td>
<td>59.74</td>
</tr>
</tbody>
</table>

Table 2.4: Coefficients for Eqs. (2.13) and (2.14).
pressure terms into the coefficients \(a_0\) and \(b_0\). To accomplish this, Eqs. (2.15) and (2.16) were fitted to equations of the same form as \(a_0\) and \(b_0\) for temperatures from 180 \(K\) to 220 \(K\). The error introduced in this procedure is negligible comparing with the experimental uncertainty. The new ternary vapor pressure equations now read [40]

\[
\begin{align*}
\log P_{HNO_3} &= \log x + a'_0 + a_1(1 - x - y) - a_2[\exp(1 - y)^8 - 1] \quad (2.17) \\
\log P_{H_2O} &= \log(1 - x - y) + b'_0 + b_1(x + y) + b_2(x + y)^2 - b_3[\exp(1 - y)^8 - 1] \quad (2.18)
\end{align*}
\]

where the new coefficients \(a'_0\) and \(b'_0\) are

\[
\begin{align*}
a'_0 &= 12.908 - \frac{2738.7}{T} \quad (2.19) \\
b'_0 &= 12.116 - \frac{3208.8}{T} \quad (2.20)
\end{align*}
\]

Owing to the limited number of measurements used for the parameterization, the use of Eqs. (2.17) and (2.18) for the calculation of the equilibrium composition has to be confined to a certain ranges of \(P_{H_2O}\), \(P_{HNO_3}\) and \(T\).

In order to make it easier to visualize the range of validity of \(P_{H_2O}\) and \(P_{HNO_3}\), the calculated ternary vapor pressures (in log scale) are shown in Figure 2-5 to 2-16 as a function of \(x\) and \(y\) for temperature ranges from 220 \(K\) to 180 \(K\). The numerical method used for the calculation of \(x\) and \(y\) will be discussed in detail in the next section. It is obvious from the contour plots in these figures that both \(P_{HNO_3}\) and \(P_{H_2O}\) decrease exponentially with the temperature within the range considered here. This is, of course, due to the temperature dependence of the coefficients \(a_i\) and \(b_i\) in Eqs. (2.13) and (2.14). Unlike \(P_{HNO_3}\), which increases monotonically with both \(x\) and \(y\), \(P_{H_2O}\) somehow exhibits a maximum in the vicinity of small \(x\) and \(y\).

This peculiarity is probably an artifact of the parameterization and hence has no physical meaning at all. It is, however, important to demonstrate that it does not pose any serious problem under the conditions we are interested in. In Figure 2-17,
Figure 2-5: Contour plot of the calculated vapor pressure of nitric acid in logarithmic scale ($\log P_{HNO_3}$ in torr) at $T = 220K$.

Figure 2-6: Contour plot of the calculated vapor pressure of water in logarithmic scale ($\log P_{H_2O}$ in torr) at $T = 220K$. 
Figure 2-7: Contour plot of the calculated vapor pressure of nitric acid in logarithmic scale \((\log P_{HNO_3} \text{ (in torr)})\) at \(T = 210K\).

Figure 2-8: Contour plot of the calculated vapor pressure of water in logarithmic scale \((\log P_{H_2O} \text{ (in torr)})\) at \(T = 210K\).
Figure 2-9: Contour plot of the calculated vapor pressure of nitric acid in logarithmic scale ($\log P_{\text{HNO}_3(\text{in torr})}$) at $T = 200K$.

Figure 2-10: Contour plot of the calculated vapor pressure of water in logarithmic scale ($\log P_{\text{H}_2\text{O}(\text{in torr})}$) at $T = 200K$. 
Figure 2-11: Contour plot of the calculated vapor pressure of nitric acid in logarithmic scale ($\log P_{HNO_3}$ in torr) at $T = 195K$.

Figure 2-12: Contour plot of the calculated vapor pressure of water in logarithmic scale ($\log P_{H_2O}$ in torr) at $T = 195K$. 
Figure 2-13: Contour plot of the calculated vapor pressure of nitric acid in logarithmic scale ($\log P_{HNO_3}$ (in torr)) at $T = 190K$.

Figure 2-14: Contour plot of the calculated vapor pressure of water in logarithmic scale ($\log P_{H_2O}$ (in torr)) at $T = 190K$. 
Figure 2-15: Contour plot of the calculated vapor pressure of nitric acid in logarithmic scale \( \log P_{HNO_3}(\text{torr}) \) at \( T = 180K \).

Figure 2-16: Contour plot of the calculated vapor pressure of water in logarithmic scale \( \log P_{H_2O}(\text{torr}) \) at \( T = 180K \).
Table 2.5: Scenarios used for the calculations in Figure 2-17. The ambient atmospheric pressure is assumed to be 100 mbar (≈16 km).

<table>
<thead>
<tr>
<th>Scenario</th>
<th>S1</th>
<th>S2</th>
<th>S3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_{HNO_3}$ (ppb)</td>
<td>5</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>$P_{H_2O}$ (ppm)</td>
<td>5</td>
<td>10</td>
<td>1</td>
</tr>
</tbody>
</table>

the weight fraction of sulfuric acid ($y$) is plotted against the weight fraction of nitric acid ($x$) for 3 typical stratospheric conditions (refer to Table 2.5). The ratio of $P_{HNO_3}$ to $P_{H_2O}$ covers the range from 0.1 to 10. In other words, the region enclosed within the upper and the lower curves in Figure 2-17 should cover almost all the possible conditions in the lower winter stratosphere. By simply comparing Figure 2-17 with the vapor pressure contour plots (Figure 2-5 to 2-16) at the appropriate temperature, we can see immediately that the maximum in the $P_{H_2O}$ plots does not fall into the region of stratospheric interests and hence the use of Eqs. (2.17) and (2.18) for the estimation of $x$ and $y$ is justified.

Another important issue that needs to be tackled before we can make use of Eqs. (2.17) and (2.18) is the large mean uncertainty which can result in the predicted values of $x$ and $y$ from the relatively small errors in the measured values of $P_{HNO_3}$, $P_{H_2O}$ and $T$. The problem can be clearly illustrated by rewriting Eqs. (2.17) and (2.18) in the following derivative form:

$$\frac{dP_i}{P_i} = \mathcal{A}_i \frac{d\mathcal{A}_i}{\mathcal{A}_i} \quad (2.21)$$

where

$$\mathcal{A}_{HNO_3} = \ln x + \ln 10\{a'_0 + a_1(1 - x - y) - a_2[\exp(1 - y)^8 - 1]\} \quad (2.22)$$

$$\mathcal{A}_{H_2O} = \ln(1 - x - y) + \ln 10\{b'_0 + b_1(x + y) + b_2(x + y)^2 - b_3[\exp(1 - y)^8 - 1]\}. \quad (2.23)$$

The above equation simply states that the fractional error in the predicted value of $P_i$
Figure 2-17: Weight fraction of sulfuric acid \( y \) as a function of the weight fraction of nitric acid \( x \) for 3 different stratospheric conditions (refer to Table 2.5).

is equal to the fractional error of \( A_i \) multiplied by \( A_i \) itself. As long as \( dx \) and \( dy \) are small when compared with their absolute values, \( dA_i \) can be estimated by applying the definition of partial differentials,

\[
dA_i = \frac{\partial A_i}{\partial x} dx + \frac{\partial A_i}{\partial y} dy + \frac{\partial A_i}{\partial T} dT
\]  

(2.24)

where

\[
\frac{\partial A_{HNO_3}}{\partial x} = \frac{1}{x} - a_1 \ln 10
\]  

(2.25)

\[
\frac{\partial A_{HNO_3}}{\partial y} = \ln 10\{-a_1 + 8a_2(1 - y)^7 \exp(1 - y)^8\}
\]  

(2.26)

\[
\frac{\partial A_{HNO_3}}{\partial T} = \frac{\ln 10}{T^2} \{2738.7 + 685.5(1 - x - y) + 189.9[\exp(1 - y)^8 - 1]\}
\]  

(2.27)

\[
\frac{\partial A_{H_2O}}{\partial x} = \frac{1}{x + y - 1} + \ln 10\{b_1 + 2b_2(x + y)\}
\]  

(2.28)

\[
\frac{\partial A_{H_2O}}{\partial y} = \frac{1}{x + y - 1} + \ln 10\{b_1 + 2b_2(x + y) + 8b_3(1 - y)^7 \exp(1 - y)^8\}
\]  

(2.29)
\[
\frac{\partial \Delta_{H_2O}}{\partial T} = \frac{\ln 10}{T^2} \left\{ 3208.8 - 3466(x + y) + 4224(x + y)^2 - 59.74[\exp(1 - y)^8 - 1] \right\}.\] (2.30)

As expected, \(dA_i\) depends strongly upon the values of \(x, y\) and \(T\). Assuming that no significant errors were introduced during the parameterization of Eqs. (2.17) and (2.18), we can use the uncertainty estimation of Zhang[41] for our calculation: \(dT \approx 0.2K\) and \(dA_i \approx 0.1\). To simplify the calculation, Eqs. (2.21) and (2.24) are rearranged in the following form:

\[
dx = \frac{\left[ \frac{\partial \Delta_{H_2O}}{\partial y} - \frac{\partial \Delta_{HNO_3}}{\partial y} \right] dA - \left[ \frac{\partial \Delta_{H_2O}}{\partial y} \frac{\partial \Delta_{HNO_3}}{\partial T} - \frac{\partial \Delta_{HNO_3}}{\partial y} \frac{\partial \Delta_{H_2O}}{\partial T} \right] dT}{\left[ \frac{\partial \Delta_{H_2O}}{\partial y} \frac{\partial \Delta_{HNO_3}}{\partial x} - \frac{\partial \Delta_{HNO_3}}{\partial y} \frac{\partial \Delta_{H_2O}}{\partial x} \right]} (2.31)\]

\[
dy = \frac{\left[ \frac{\partial \Delta_{H_2O}}{\partial x} - \frac{\partial \Delta_{HNO_3}}{\partial x} \right] dA - \left[ \frac{\partial \Delta_{H_2O}}{\partial x} \frac{\partial \Delta_{HNO_3}}{\partial T} - \frac{\partial \Delta_{HNO_3}}{\partial x} \frac{\partial \Delta_{H_2O}}{\partial T} \right] dT}{\left[ \frac{\partial \Delta_{H_2O}}{\partial x} \frac{\partial \Delta_{HNO_3}}{\partial y} - \frac{\partial \Delta_{HNO_3}}{\partial x} \frac{\partial \Delta_{H_2O}}{\partial y} \right]} (2.32)\]

It is important at this stage to point out that Eqs. (2.31) and (2.32) can only be applied to situations where both \(dA\) and \(dT\) are relatively small comparing with their absolute values.

Plotted in Figures 2-18 to 2-23 are the absolute error in \(x\) and \(y\) as a function of temperature for Scenario S1, S2 and S3 (refer to page 45, Table 2.5) calculated using Eqs. (2.31) and (2.32). Both the positive and negative deviations of \(dA\) and \(dT\) are considered. As anticipated, the absolute errors remain small at temperature above 200 \(K\), where most of the vapor pressure data were measured [41, 49]. As the temperature approaches the dew point of nitric acid (\(T_d\)), the absolute errors increase drastically due to the highly nonlinear correction terms in the ternary vapor pressure equations (Eqs. (2.17) and (2.18)). It is also interesting to note that the absolute error in \(x\) and \(y\) for all three scenarios has the smallest value whenever \(dA\) and \(dT\) have the same sign, implying that they have the tendency to cancel each other out.
Figure 2-18: Absolute error in $x$ for Scenario S1. $(++) \equiv +\Delta i, +dT$; $(+-) \equiv +\Delta i, -dT$ etc.

Figure 2-19: Absolute error in $y$ for Scenario S1. Refer to Figure 2-18 for the legends.
Figure 2-20: Absolute error in $x$ for Scenario S2. Refer to Figure 2-18 for the legends.

Figure 2-21: Absolute error in $y$ for Scenario S2. Refer to Figure 2-18 for the legends.
Figure 2-22: Absolute error in x for Scenario S3. Refer to Figure 2-18 for the legends.

Figure 2-23: Absolute error in y for Scenario S3. Refer to Figure 2-18 for the legends.
2.3.2 Numerical Solutions

It is obvious from Eqs. (2.17) and (2.18) that both $x$ and $y$ cannot be expressed as a function of temperature in closed analytical form. Solving $x$ and $y$ numerically, on the contrary, is quite straightforward and in-depth discussion and source codes can be found in Beyer[50].

One of the main problems of finding $x$ and $y$ directly from Eqs. (2.17) and (2.18) that has not been addressed by Beyer is the existence of two solutions for the water vapor pressure equation (Eq. (2.18)) [53]. This difficulty clearly reveals itself through the appearing of the quadratic term in Eq. (2.18). Although it does not pose any serious problem in this study, it may eventually cause confusion if the two vapor pressure equations are integrated into some large scale heterogeneous chemical kinetics simulation programs since there is no clear cut guideline to differentiate the real solution from the rejected one.

To this end, an alternative method is suggested and will be used in this study for the calculation of equilibrium aerosol compositions. In the new method, Eqs. (2.17) and (2.18) are transformed into two first order nonlinear differential equations for $x$ and $y$ with respect to $T$ which are then solved with an initial boundary condition. The derivation of the differential equations is shown in Appendix A. The final forms of the two differential equations are

$$\frac{dx}{dT} = \frac{WS - VQ}{RV - SU} \tag{2.33}$$
$$\frac{dy}{dT} = \frac{QU - RW}{RV - SU} \tag{2.34}$$

where

$$R = \frac{\log e}{x} - a_1$$
$$S = 8a_2(1 - y)^7\phi - a_1$$
$$Q = \frac{da_0}{dT} + (1 - x - y)\frac{da_1}{dT} - (\phi - 1)\frac{da_2}{dT}$$
$$U = b_1 + 2b_2(x + y) - \frac{\log e}{(1 - x - y)}$$
\[
V = U + 8b_3(1 - y)^7 \phi
\]
\[
W = \frac{db_0}{dT} + (x + y)\frac{db_1}{dT} - (x + y)^2\frac{db_2}{dT} - (\phi - 1)\frac{db_3}{dT}
\]
\[
\phi = \exp(1 - y)^8
\]

This method takes advantage of the fact that at the higher end of the temperature range studied here (e.g. 210 – 220K), the rejected solution of \(y\) is always less than 0.2 while the real solution assumes value well within the range of 0.5 to 0.8, as expected. Consequently the finding of the initial value of \(y\) is nothing more than solving the two simultaneous equations (Eqs. (2.17) and (2.18)) at temperature \(\geq 210K\) and choosing the solution that satisfies the condition \(y \geq 0.2\). This way of eliminating the unwanted solution can be easily implemented through programming.

The Bulirsch-Stoer method, known for its capability of obtaining high accuracy solutions to ordinary differential equations with minimal computational effort, was employed for the integration of Eqs. (2.33) and (2.34). Routine programs `odeint`, `bsstep` and `rzextr` from "Numerical Recipe in C" [54] were called for the calculation of \(x\) and \(y\). Also calculated were the acid weight fraction ratios \(x/y\) and \(x/z\).

Shown in Figure 2-24 is a plot of \(x\) and \(y\) as a function of temperature with \(P_{H_2O} = 5\ ppmv\) and \(P_{HNO_3} = 5\ ppbv\) at 100 mbar (Scenario S1 in Table 2.5). Both the bisection and the Bulirsch-Stoer method were used for the calculation of \(x\) and \(y\). It is obvious from the plot that both methods produce practically the same results down to the nitric acid dew point \(T_d\). After the dew point, it is anticipated that the amount of \(HNO_3\) \((x)\) in the supercooled liquid aerosols will gradually decrease due to denitrification of the lower stratosphere [25].

It is important to mention at this point that the ternary vapor pressure equations as described in this and the last section should not be used to calculate the aerosol composition at temperature lower than \(T_d\). This can be seen clearly from Figure 2-25 where \(dx/dT\) and \(dy/dT\) are plotted against \(T\). Both quantities show a divergent behavior as temperature approaches \(T_d\). One of the distinctive features in Figure 2-24 is the exponential increase in \(x\) as \(y\) is approaching zero. To emphasize this point, the changes in the ratios \(x/y\) and \(x/z\) as \(T \to T_d\) are shown in Figure 2-26.
Figure 2-24: Weight percentage of $HNO_3$ and $H_2SO_4$ as a function of temperature with $P_{H_2O} = 5$ ppmv and $P_{HNO_3} = 5$ ppbv at 100 mbar (Scenario S1). The $HNO_3$ dew point is taken from Figure 2-1 and 2-3. BS: Bulirsch-Stoer method; bisect: Bisection method.

rapid increase in both quantities signifies an increasing tendency for the stratospheric aerosols to freeze. Similar analysis has also been done for other typical stratospheric conditions in Figure 2-27. The results are consistent with the predictions of other models found in the literature [55, 56].

2.3.3 Approximate Solutions

The major difficulty in interpreting numerical solutions is that in almost all the cases, the calculated quantities cannot be explicitly related to the parameters. In this particular case, the quantities that we are interested in are the weight percentages of sulfuric acid and nitric acid in the SSAs under different environmental conditions and temperature. It is obvious that the highly nonlinear correction terms introduced by Beyer in Eqs. (2.17) and (2.18) render them unsolvable analytically. Therefore, as a first step to find an approximate solution, the correction terms in the vapor pressure equations have to be ignored. As has been pointed out by Beyer [50], the effect of the
Figure 2-25: The first derivatives of $x$ (Eq. (2.33)) and $y$ (Eq. (2.34)) as a function of temperature. The conditions are the same as in Figure 2-24.

Figure 2-26: Variations of $x/y$ and $x/z$ with temperature. The conditions are the same as in Figure 2-24.
two correction terms is only noticeable at temperatures that are close to the nitric acid dew point and so neglecting them should not introduce appreciable errors at temperatures where the vapor pressures were actually measured [41]. The simplified ternary vapor pressure equations now read

\[
\ln P_{HNO_3} = \ln x + \ln 10[a_0' + a_1'(1 - z)] \tag{2.35}
\]

\[
\ln P_{H_2O} = \ln(1 - z) + \ln 10[b_3'] + b_1 z + b_2 z^2 \tag{2.36}
\]

where \( z = x + y \) is the total acid weight fraction of the ternary solution. The coefficients \( a_i \) and \( b_i \) remain the same as in Eqs. (2.13) and (2.14). Note that the natural logarithm (ln) instead of the common logarithm (log) is used in the above equations for reasons that will soon be clear. Finally, the differential form of Eqs. (2.35) and (2.36) can be obtained by simply setting \( a_2 \) and \( b_3 \) in Eqs. (2.33) and (2.34) to zero.
General Characteristics

A lot can be learned from the two simplified vapor pressure equations without actually solving them for $x$ and $y$. First of all, it is obvious from Eq. (2.36) that the total acid weight fraction $z$ depends only upon the ambient partial pressure of $H_2O$ and the temperature. Doubling the amount of $HNO_3$ in the stratosphere therefore should not significantly alter the weight fraction of $H_2O$ in the aerosol droplets. The only quantity that would have been changed is the ratio of the weight fractions of $H_2SO_4$ to $HNO_3$ in the aerosols. This point is clearly shown in Figure 2-28, 2-29 and 2-30 where the weight percentage of $H_2O$ is plotted as a function of temperature for different values of $P_{HNO_3}$ and the same $P_{H_2O}$. It can be seen that all the data points of $w$ collapse into one single curve until the correction term becomes noticeable, as illustrated in the figures by the curves calculated without the correction term.

Another observation that is worth mentioning is that the weight fraction of nitric acid in the aerosols is roughly proportional to the first power of $P_{HNO_3}$. As is predicted by Eq. (2.35), a plot of $x$ against $P_{HNO_3}$ should be a straight line passing through the zero coordinates with slope controlled by both the temperature and $P_{H_2O}$. In order to see how well Eqs. (2.35) and (2.36) are in replacing the original equations, nitric acid weight fraction ($x$) calculated numerically using Eqs. (2.13) and (2.14) for various $P_{H_2O}$ and $T$ are plotted against $P_{HNO_3}$ in Figures 2-31 to 2-34. The figures have clearly demonstrated the validity of the linear approximation for the whole range of $P_{H_2O}$ and $P_{HNO_3}$ down to temperature close to $T_d$.

Reversion of Power Series

By expressing the logarithmic term $\ln(1-z)$ in Eq. (2.36) into a power series, we can define a new function $\xi(z)$ as follows:

$$\xi(z) = \ln P_{H_2O} - b'_0 \ln 10 = C_1 z + C_2 z^2 + \sum_{i=3}^{\infty} C_i z^i$$

(2.37)
Figure 2-28: Weight percentage of $H_2O$ as a function of temperature with $P_{H_2O} = 1$ ppmv and $P_{HNO_3}$ varying from 1 to 10 ppbv at 100 mbar. (w/o) $\equiv w$ calculated without the correction term.
Figure 2-29: Weight percentage of $H_2O$ as a function of temperature with $P_{H_2O} = 5$ ppmv and $P_{HNO_3}$ varying from 1 to 10 ppbv at 100 mbar. (w/o) ≡ $w$ calculated without the correction term.
Figure 2-30: Weight percentage of $H_2O$ as a function of temperature with $P_{H_2O} = 10$ ppmv and $P_{HNO_3}$ varying from 1 to 10 ppbv at 100 mbar. (w/o) ≡ w calculated without the correction term.
Figure 2-31: Dependence of the weight percentage of $HNO_3$ ($x$) on the partial pressure of $HNO_3$ ($P_{na}$) at 220K and atmospheric pressure of 100 mbar.
Temp = 210 K

Figure 2-32: Dependence of the weight percentage of \( HNO_3 \) \((x)\) on the partial pressure of \( HNO_3 \) \((P_{na})\) at 210\(K\) and atmospheric pressure of 100 \( mbar \).
Temp = 200 K

![Graph](image)

Figure 2-33: Dependence of the weight percentage of HNO₃ (x) on the partial pressure of HNO₃ (Pₙa) at 200K and atmospheric pressure of 100 mbar.
Figure 2-34: Dependence of the weight percentage of $HNO_3$ ($x$) on the partial pressure of $HNO_3$ ($P_{na}$) at $T \approx T_d$ and atmospheric pressure of 100 mbar.
where

\[
C_1 = b_1 \ln 10 - 1 \\
C_2 = b_2 \ln 10 - \frac{1}{2} \\
C_i = \frac{1}{i}
\]

The only requirement is that \( \xi(z) \) must be convergent in the range \( 0 \leq z \leq 1 \). Note that only \( C_1 \) and \( C_2 \) in Eq. (2.37) are functions of temperature. As \( C_i (i \geq 3) \) is a rapidly decreasing function of \( i \), it can be easily proved that the dominant terms in the infinite series in Eq. (2.37) are \( C_1 \) and \( C_2 \). The infinite series can also be expressed in a reversible form as long as \( C_1 \neq 0 \) [57]:

\[
z(\xi) = \alpha_1 \xi + \alpha_2 \xi^2 + \alpha_3 \xi^3 + \ldots = \sum_{i=1}^{\infty} \alpha_i \xi^i \tag{2.38}
\]

where

\[
\begin{align*}
\alpha_1 &= \frac{1}{C_1} \\
\alpha_2 &= -\frac{C_2}{C_1^3} \\
\alpha_3 &= \frac{2C_2^2 - C_1 C_3}{C_1^5} \\
\alpha_4 &= \frac{5C_1 C_2 C_3 - 5C_2^3 - C_1^2 C_4}{C_1^7} \quad \text{etc.}
\end{align*}
\]

Unfortunately, the calculation soon becomes too complicated to convey any clear idea of the relationship between \( z \) and \( \xi \). Also, it appears that the radius of convergence for the series in Eq. (2.38) depends not just on temperature but also on \( P_{H_2O} \) as well.

In order for the series to converge, the following condition must be satisfied

\[
\xi = \ln P_{H_2O} - b_0' \ln 10 \leq 1 \tag{2.39}
\]

or

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For the temperature range considered here, it translates to
\[
P_{H_2O} \leq e^{10^6}
\] (2.40)

For the temperature range considered here, it translates to

\[
P_{H_2O} \leq 7.2 \times 10^{-6} \text{ mbar} \quad \text{at } T = 180K
\]
\[
P_{H_2O} \leq 1.3 \times 10^{-2} \text{ mbar} \quad \text{at } T = 220K
\]

In the stratosphere under normal conditions, the partial pressure of \(H_2O\) is of the order of \(10^{-4} \text{ mbar}\) and so the series shown in Eq. (2.38) does not converge for the whole range of temperature considered here.

**Quadratic Approximation**

For infinite series similar to the one in Eq. (2.37), it is always possible to simplify it by truncating the higher order terms. The number of terms that should be retained depends primarily on the relative magnitude of the coefficients \(C_i\). As already mentioned in the last section, the only two dominant terms in the infinite series are \(C_1\) and \(C_2\). Hence, as a first approximation, Eq. (2.37) can be written in the following quadratic form:

\[
(b_2 \ln 10 - \frac{1}{2})z^2 + (b_1 \ln 10 - 1)z + (b_0' \ln 10 - \ln P_{H_2O}) + O(z^3, z^4, ...) = 0. \quad (2.41)
\]

The solution for this equation then gives the *approximated total acid weight fraction*, \(z^{(2)}\)

\[
z^{(2)} = \frac{(1 - b_1 \ln 10) \pm \sqrt{(b_1 \ln 10 - 1)^2 - 4(b_2 \ln 10 - \frac{1}{2})(b_0' \ln 10 - \ln P_{H_2O})}}{2(b_2 \ln 10 - \frac{1}{2})} \quad (2.42)
\]

By substituting the numerical values of \(b_i\) (listed in Table 2.4) into Eq. (2.42), we have

\[
z^{(2)} = \frac{24.428 - \frac{7980.1}{T} \pm \Delta}{47.594216 - \frac{19449.936}{T}} \quad (2.43)
\]
where

\[ \Delta = \sqrt{(95.188 \ln P_{H_2O} - 2152.6) + \frac{1430569.5 - 38899.872 \ln P_{H_2O}}{T}} - \frac{223727086.8}{T^2} \]  \hspace{1cm} (2.44)

The approximated weight fraction of water \( w^{(2)}(= 1 - z^{(2)}) \) can be expressed in a similar form

\[ w^{(2)} = \frac{\left( 23.16661T - 11469.867 \right) \pm \sqrt{aT^2 + bT + c}}{47.594216T - 19449.936} \]  \hspace{1cm} (2.45)

where

\[ a = 95.188 \ln P_{H_2O} - 2152.6 \]
\[ b = 1430569.5 - 38899.872 \ln P_{H_2O} \]
\[ c = -223727086.8 \]

In order to have a real value for \( w^{(2)} \), the discriminant \((det)\) in Eq. (2.45) has to be positive, i.e.

\[ det = aT^2 + bT + c \geq 0 \]  \hspace{1cm} (2.46)

This condition immediately sets a lower temperature limit \( T_l \) of applicability for Eq. (2.45) (see Table 2.6). After rejecting the unrealistic solution \( T_1^+ \), it is found that \( T_1^- (= T_l) \) is always less than the nitric acid condensation temperature \( T_d \) for the whole range of \( P_{HNO_3} \) and \( P_{H_2O} \) considered in this study (refer to Figure 2-2 for the value of \( T_d \)) and hence Eq. (2.45) should be applicable to temperature as low as \( T_d \).

To account for the error introduced by the elimination of the correction term in Eq. (2.18), the following simple assumption can be made. Firstly, let \( w^{(\infty)} \) be the true value of \( w^7 \), i.e.

\[ w^{(\infty)} = w^{(2)} + \Delta w^{(2)} = w^{(2)} \left[ 1 + \frac{\Delta w^{(2)}}{w^{(2)}} \right] \]  \hspace{1cm} (2.47)

where \( \Delta w^{(2)} \) is the error inherent in the quadratic solution (Eq. (2.45)). And then with

\[ \text{Here the numerically calculated value of } w \text{ is regarded as } w^{(\infty)}. \]
<table>
<thead>
<tr>
<th>$P_{H_2O}$ (ppmv)</th>
<th>$T_i^+(K)$</th>
<th>$T_i^-(K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>410.79</td>
<td>184.49</td>
</tr>
<tr>
<td>5</td>
<td>410.50</td>
<td>187.55</td>
</tr>
<tr>
<td>8</td>
<td>410.91</td>
<td>190.46</td>
</tr>
<tr>
<td>10</td>
<td>410.95</td>
<td>191.87</td>
</tr>
</tbody>
</table>

Table 2.6: Lower temperature limit ($T_i$) for Eq. (2.45) under typical stratospheric level of $P_{H_2O}$.

the postulate that $\Delta w^{(2)}(\ll w^{(2)})$ is a weak function of $T$ and $P_{H_2O}$, the approximation

$$w^{(\infty)} = w^{(2)}(1 + \beta^{(2)})$$  \hspace{1cm} (2.48)

where $\beta^{(2)}$ is a constant much smaller than 1, can be used to replace Eq. (2.47). Figure 2-35 and 2-36 are plots of $w$ (calculated numerically) against $T$ for 5 and 10 ppbv $HNO_3$, respectively, at $\sim 100$ mbar. In both plots, $P_{H_2O}$ has values ranging from 3 ppmv to 10 ppmv. Also plotted are the values of $w^{(\infty)}$ calculated using Eq. (2.48). It has been found that the best fitted value for $\beta^{(2)}$ is 0.15, in consistent with the above assumption.

### 2.4 Heterogeneous Processing of Ternary Aerosols

The two most crucial parameters in determining the extent of chemical processing by liquid sulfate aerosols are the particle surface area ($A_T$) and the heterogeneous reaction probability ($\gamma$). As mentioned previously, both of these two quantities depend strongly upon the chemical composition of the aerosols. Recent theoretical analyses [56, 55] have clearly demonstrated the significance of the liquid aerosol model in explaining field measurement data. Emphasis is usually placed on the rapid but smooth increase in the volume of the stratospheric aerosols. In this section, the stratospheric applications of Eq. (2.48) on heterogeneous processing are briefly discussed with particular attention focused on $A_T$ and $\gamma$. 
Figure 2-35: Weight percentage of $H_2O$ ($w$) as a function of temperature with $P_{na} (\equiv P_{HNO_3}) = 5$ ppbv and an atmospheric pressure of 100 mbar. $P_{H_2O}$ ranges from 3 to 10 ppmv. BS $\equiv$ numerically calculated values; cal $\equiv$ quadratic approximation calculated using Eq. (2.48).
Figure 2-36: Weight percentage of $H_2O$ (w) as a function of temperature with $P_{na}(\equiv P_{HNO_3}) = 10$ ppbv and an atmospheric pressure of 100 mbar. $P_{H_2O}$ ranges from 3 to 10 ppmv. BS $\equiv$ numerically calculated values; cal $\equiv$ quadratic approximation calculated using Eq. (2.48).
Particle Surface Area

An accurate estimation of the total particle surface area \( (A_T) \) requires the knowledge of the aerosol size distribution. However, as a rough estimation, the average value of the particle size can be used instead. For an aerosol particle with a fixed amount of H\(_2\)SO\(_4\) \( (m_{sa}) \), the average particle volume can be expressed as follows

\[
V_T = \frac{m_{sa}}{\rho(x,y) y},
\]

where \( \rho(x,y) \) is the mass density of the liquid aerosols. The legitimate value of \( \rho(x,y) \) varies from 1 g/cm\(^3\) (pure water) to 1.83 g/cm\(^3\) (pure sulfuric acid) while \( y \) can be calculated using \( z^{(\infty)}(=x^{(\infty)}+y) \) and Eq. (2.35)

\[
y = z^{(\infty)} - P_{HNO_3}10^{-a_0-a_1(1-z^{(\infty)})}. \tag{2.50}
\]

The average particle surface area can also be written in a similar form:

\[
A_T = \frac{3m_{sa}}{\bar{r}\rho(x,y) y} \tag{2.51}
\]

where \( \bar{r} \) is the average radius of the aerosols. For the sake of simplicity, \( \rho(x,y) \) and \( m_{sa} \) are assumed to be 1.6 g/cm\(^3\) and 10\(^{-11}\) g respectively.

Shown in Figure 2-37 are the calculated values of \( V_T \) and \( A_T \) versus temperature \( T \). The conditions used in the calculations are quite similar to those suggested in reference [56]. As can be seen in Eq. (2.49), the aerosol volume is inversely proportional to \( y \) (assuming a constant \( \rho \)) which itself is a rapidly decreasing function of temperature (refer to Figures 2-24 and 2-27). The faster than exponential decrease in \( y \) makes the temperature a much more important factor to consider than the mass of sulfuric acid \( (m_{sa}) \) during heterogeneous modeling. Although Eq. (2.51) has an extra term \( (\bar{r}) \) in the denominator which increases with decreasing temperature, it appears from Figure 2-37 that \( A_T \) still increases as fast as \( V_T \) does.
Figure 2-37: Aerosol volume and surface area as a function of temperature with $P_{H_2O} = 3$ ppmv and $P_{HNO_3}$ varying from 3 to 5 ppbv at 100 mbar level. The density and sulfuric acid mass are assumed to be 1.6 g/cm$^3$ and $10^{-11}$g respectively.

**Heterogeneous Reaction Probability**

Reactions that contribute directly to the active chlorine loading (e.g. $Cl_2$ and $HOCl$) in the lower stratosphere are generally considered to be potentially more important. The realization of the possible role of the sulfate aerosols in converting inactive chlorine (or bromine) to its active forms has shifted a lot of attention to the study of heterogeneous chemistry on supercooled liquid aerosols. Recent experiments on the supercooling property of the sulfate aerosols at temperatures slightly higher than the ice frost point [56, 25] have further verified the significance of liquid aerosols in the depletion of polar ozone.

The reaction probability for the heterogeneous reaction (γ) of $ClONO_2$ and $H_2O$ on/in the binary sulfuric acid solution was first measured by Tolbert et al. [32] and then later by Hanson and Ravishankara [58]. The results show that for $w$ ranging from 0.25 to 0.60, γ depends exponentially on $w$

$$
\gamma = 2.56 \times 10^{-6} \exp \left[ \frac{w}{0.05845} \right]. \tag{2.52}
$$
Recently, Zhang et al. [59] demonstrated that within their experimental errors, the presence of $HNO_3$ in the cold sulfuric acid solution did not change $\gamma$ significantly for heterogeneous reactions of $ClONO_2$, $HOCl$ and $HCl$. If the same conclusion can be applied to the case of $ClONO_2$ and $H_2O$, Eqs. (2.48) and (2.52) can be used to estimate $\gamma$ for the ternary acid system, i.e.

$$\gamma = 2.56 \times 10^{-6} \exp \left[ \frac{\omega^{(\infty)}}{0.05845} \right].$$

(2.53)

The above equation suggests a rather complicated relationship between $\gamma$ and $P_{H_2O}$ for the ternary $H_2SO_4/HNO_3/H_2O$ acid system, in contrary to the simple exponential dependence for the case of binary $H_2SO_4/H_2O$. 

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Chapter 3

Physico-chemical Data of Stratospheric Sulfate Aerosols

3.1 Introduction

The formation of aerosol particles with two or more components can be studied using either the equilibrium phase diagram or heteromolecular homogeneous nucleation theory. The former method has often been used as a first attempt to identify all the possible condensates under different atmospheric conditions. The only criterion for the stability of aerosols by this approach is the achievement of equilibrium between the actual partial pressures of the components in the gas phase and their vapor pressures in the liquid phase. As a general rule, the aerosols are assumed to be stable when the ambient partial pressures of all the components are larger than or equal to their corresponding vapor pressures in a bulk mixture of a specific composition. This simple but effective method was used in the last chapter for the estimation of the equilibrium composition of SSAs.

The disadvantage of the equilibrium phase diagram method is the requirement of the presence of sufficient amount of condensation nuclei in the atmosphere (i.e. heterogeneous nucleation) since no kinetic factors are considered during the analysis. In order to understand the direct transformation of trace species from the gas phase to the condensed phase, one has to rely on the heteromolecular homogeneous
nucleation theory. Unfortunately, this theory requires the knowledge of some not so well-known thermodynamic data such as surface tension and specific volume. For instance, the dependence of the nucleation rate on surface tension is so critical that a small uncertainty in the surface tension can lead to an error of orders of magnitude in the nucleation rate.

Intuitively, one would consider the homogeneous nucleation theory as more appropriate for the study of the formation of SSAs due to the fact that the lower stratosphere is "relatively" clean when compared with the troposphere. However, the persistent presence of sulfuric acid in that region makes the use of the equilibrium phase diagram method plausible since the vapor pressure of sulfuric acid at stratospheric temperatures is so low that the stratsphere is always supersaturated with respect to sulfuric acid. Besides, the affinity of sulfuric acid for water can also play a role in stabilizing the acid condensate in the lower stratosphere.

3.2 Estimation of Ternary Physico-chemical Data

As mentioned above, the studies of aerosol nucleation and growth require the knowledge of equilibrium vapor pressures, bulk density and surface tension. Unfortunately, for most of the aqueous ternary systems found in the atmosphere, these kinds of physico-chemical data, particularly at stratospheric temperatures, are largely lacking. On the other hand, physico-chemical data for binary systems H$_2$SO$_4$/H$_2$O and HNO$_3$/H$_2$O are well-documented[60, 61, 62]. In this section, both the density and surface tension of the ternary H$_2$SO$_4$/HNO$_3$/H$_2$O system are estimated by applying simple rules of mixture. Also a set of more generalized Kelvin equations, based on the revised nucleation theory, is derived for the ternary system.

3.2.1 Modified Kelvin Equation

The key aspect that characterizes the thermodynamic properties of small aerosol particles is their curved interface with the air. For instance, the elevation of the saturation vapor pressure of a droplet of pure water (radius $r$) due to the presence of
this curved interface can be evaluated by the well-known Kelvin equation [63]:

\[
P_{H_2O}^r = P_{H_2O}^\infty \exp \left[ \frac{2\sigma \bar{v}}{RT \gamma} \right]
\]

(3.1)

where \( P_{H_2O}^\infty \) is the vapor pressure of pure water over a flat water surface at temperature \( T \), \( \sigma \) is the surface tension, \( R \) the gas constant and \( \bar{v} (= M_{H_2O}/\rho, \) where \( M_{H_2O} \) is the molecular weight of water and \( \rho \) its density) represents the molar volume of water under the same conditions. \( \sigma \) can also be defined as the free energy per unit area of the interface separating the condensed and vapor phases. It is obvious from Eq. (3.1) that as the aerosol droplet radius increases, the exponential term in Eq. (3.1) approaches unity, i.e. the saturation vapor pressure becomes that for a plane surface. Generally, the particle growth rate is determined by the difference in ambient and saturation vapor densities and hence the kelvin effect can serve to segregate the particle population into two groups: a large, growing particle group and a small, shrinking particle group. In other words, Eq. (3.1) is crucial in determining the stability of submicron-sized volatile particles in the free atmosphere.

Nair and Vohra[64] published a similar set of vapor pressure equations in 1975 for the \( H_2SO_4/H_2O \) binary system which includes the correction terms for the composition dependence of density and surface tension. They demonstrated that the relative increases in particle size and mass depend strongly on the solute dry mass (i.e. the mass of \( H_2SO_4 \)). In this section, we derive a similar set of modified Kelvin equations for the three component system which also takes the variation of solution density and surface tension with composition into account. The derivation of the same set of equations for a n-component system can be found in Appendix B.

The Gibbs free energy of formation of a single, stationary liquid droplet containing \( n_{sa} \) moles of \( H_2SO_4 \), \( n_{na} \) moles of \( HNO_3 \) and \( n_w \) moles of \( H_2O \) can be written as

\[
\Delta G = n_w (\mu_w^l - \mu_w^g) + n_{na} (\mu_{na}^l - \mu_{na}^g) + n_{sa} (\mu_{sa}^l - \mu_{sa}^g) + 4\pi r^2 \sigma
\]

(3.2)

where \( \mu_{na}^l, \mu_{sa}^l \) and \( \mu_w^l \) are the chemical potentials of \( HNO_3, H_2SO_4 \) and \( H_2O \), respectively, in the liquid droplet phase. \( \mu_{na}^g, \mu_{sa}^g \) and \( \mu_w^g \) are the corresponding chemical
potentials of the components in the gas phase in equilibrium with the droplet of radius \( r \) and \( \sigma \) is the surface energy of the ternary acid droplet. At equilibrium, the following conditions must be satisfied

\[
\left( \frac{\partial \Delta G}{\partial n_w} \right)_{n_{na}, n_{sa}} = 0
\]
\[
\left( \frac{\partial \Delta G}{\partial n_{na}} \right)_{n_{sa}, n_w} = 0
\]
\[
\left( \frac{\partial \Delta G}{\partial n_{sa}} \right)_{n_w, n_{na}} = 0
\]

After evaluating the partial differentiations and setting them to zero, we have

\[
\mu_w' - \mu_w^g + 8\pi r \sigma \frac{\partial r}{\partial n_w} = 0 \quad (3.3)
\]
\[
\mu_{na}' - \mu_{na}^g + 8\pi r \sigma \frac{\partial r}{\partial n_{na}} = 0 \quad (3.4)
\]
\[
\mu_{sa}' - \mu_{sa}^g + 8\pi r \sigma \frac{\partial r}{\partial n_{sa}} = 0 \quad (3.5)
\]

Since the droplet density is much more easier to measure, we relate \( \partial r/\partial n_w \) to \( \partial \rho/\partial n_w \) through the definition of \( \rho \):

\[
\frac{4}{3} \pi r^3 \rho = n_w M_w + n_{na} M_{na} + n_{sa} M_{sa} \quad (3.6)
\]

where \( M_i \) is the molecular weight of species \( i \). Differentiating the above equation with respect to \( n_w \) gives

\[
\frac{4\pi}{3} \left( 3\rho r^2 \frac{\partial r}{\partial n_w} + r^3 \frac{\partial \rho}{\partial n_w} \right) = M_w \quad (3.7)
\]
or after rearranging,

\[
\frac{\partial r}{\partial n_w} = \left( M_w - \frac{4}{3} \pi r^3 \frac{\partial \rho}{\partial n_w} \right) \frac{1}{4\pi r^2 \rho} \quad (3.8)
\]

Similarly for \( n_{na} \) and \( n_{sa} \), we have

\[
\frac{\partial r}{\partial n_{na}} = \left( M_{na} - \frac{4}{3} \pi r^3 \frac{\partial \rho}{\partial n_{na}} \right) \frac{1}{4\pi r^2 \rho} \quad (3.9)
\]
It is generally much more convenient to express the droplet density as a function of weight fraction. Depending on the variable chosen, the total differential of \( \rho \) can be written in the following two forms:

\[
dp{x_w, x_{na}} = \frac{\partial \rho}{\partial x_w} dx_w + \frac{\partial \rho}{\partial x_{na}} dx_{na} \tag{3.11}
\]

and

\[
dp{n_w, n_{na}, n_{sa}} = \frac{\partial \rho}{\partial n_w} dn_w + \frac{\partial \rho}{\partial n_{na}} dn_{na} + \frac{\partial \rho}{\partial n_{sa}} dn_{sa} \tag{3.12}
\]

Note that any two of the three component weight fractions can be used as variables in Eq. (3.11). Since both \( x_w \) and \( x_{na} \) are functions of \( n_w, n_{na} \) and \( n_{sa} \), we can write

\[
dx_w = \frac{\partial x_w}{\partial n_w} dn_w + \frac{\partial x_w}{\partial n_{na}} dn_{na} + \frac{\partial x_w}{\partial n_{sa}} dn_{sa} \tag{3.13}
\]

\[
dx_{na} = \frac{\partial x_{na}}{\partial n_w} dn_w + \frac{\partial x_{na}}{\partial n_{na}} dn_{na} + \frac{\partial x_{na}}{\partial n_{sa}} dn_{sa} \tag{3.14}
\]

Substituting Eqs. (3.13) and (3.14) into Eq. (3.11) and comparing it with Eq. (3.12) then gives

\[
\frac{\partial \rho}{\partial n_w} = \frac{\partial \rho}{\partial x_w} \frac{\partial x_w}{\partial n_w} + \frac{\partial \rho}{\partial x_{na}} \frac{\partial x_{na}}{\partial n_w} \tag{3.15}
\]

\[
\frac{\partial \rho}{\partial n_{na}} = \frac{\partial \rho}{\partial x_w} \frac{\partial x_w}{\partial n_{na}} + \frac{\partial \rho}{\partial x_{na}} \frac{\partial x_{na}}{\partial n_{na}} \tag{3.16}
\]

\[
\frac{\partial \rho}{\partial n_{sa}} = \frac{\partial \rho}{\partial x_w} \frac{\partial x_w}{\partial n_{sa}} + \frac{\partial \rho}{\partial x_{na}} \frac{\partial x_{na}}{\partial n_{sa}} \tag{3.17}
\]

The weight fractions of \( H_2O \) and \( HNO_3 \) are defined as follows:

\[
x_w = \frac{n_w M_w}{M_T} \tag{3.18}
\]

\[
x_{na} = \frac{n_{na} M_{na}}{M_T} \tag{3.19}
\]
where

\[
M_T = n_w M_w + n_{na} M_{na} + n_{sa} M_{sa}
\]  

(3.20)

is the total mass of the ternary droplet. Differentiating the above two equations with respect to \( n_i \) gives, in general (See Appendix B)

\[
\frac{\partial x_i}{\partial n_i} = \frac{M_i(1 - x_i)}{M_T}
\]

(3.21)

\[
\frac{\partial x_i}{\partial n_j} = -\frac{M_j x_i}{M_T}
\]

(3.22)

with \( i \neq j \). Applying them to Eqs. (3.15) - (3.17), we have

\[
\frac{\partial \rho}{\partial n_{w}} = -\frac{3M_w}{4\pi r^3 \rho} \left[ (x_w - 1) \frac{\partial \rho}{\partial x_w} + x_{na} \frac{\partial \rho}{\partial x_{na}} \right]
\]

(3.23)

\[
\frac{\partial \rho}{\partial n_{na}} = -\frac{3M_{na}}{4\pi r^3 \rho} \left[ x_w \frac{\partial \rho}{\partial x_w} + (x_{na} - 1) \frac{\partial \rho}{\partial x_{na}} \right]
\]

(3.24)

\[
\frac{\partial \rho}{\partial n_{sa}} = -\frac{3M_{sa}}{4\pi r^3 \rho} \left[ x_w \frac{\partial \rho}{\partial x_w} + x_{na} \frac{\partial \rho}{\partial x_{na}} \right]
\]

(3.25)

The above derivation is quite general and can be applied to any thermodynamic parameter as long as it depends explicitly on the composition of the solution mixture.

It is essential that the chemical potential terms in Eqs. (3.3) to (3.5) be expressed in some experimentally accessible parameters. Starting from the ideal gas law and ignoring the volume of the condensed phase, we end up with the following standard thermodynamic relationship

\[
\mu_i - \mu_i^0 = -RT \ln \frac{S_i}{A_i}
\]

(3.26)

where \( S_i (= P_i^e / P_i^0) \) and \( A_i (= P_i^\infty / P_i^0) \) are the saturation ratio and activity of component \( i \) respectively. In the above definitions for \( S_i \) and \( A_i \), \( P_i^e \) is the equilibrium vapor pressure of species \( i \) over a solution droplet with radius \( r \) while \( P_i^c \) and \( P_i^\infty \) are the equilibrium vapor pressures of \( i \) over a flat surface of pure \( i \) and solution mixtures respectively. At thermodynamic equilibrium, \( P_i^e \) should be equal to the ambient partial pressure of component \( i \) \( (P_i) \).
Combining Eqs. (3.3) - (3.5), (3.8) - (3.10) and (3.23) - (3.25) with the above thermodynamic equation, we come to three final expressions for our $H_2SO_4/HNO_3/H_2O$ ternary system:

\[
\begin{align*}
\ln P_{H_2O}^r &= \frac{2M_{H_2O}\sigma}{RT \rho} \left\{ 1 + \frac{1}{\rho} \left[ (x_w - 1) \frac{\partial \rho}{\partial x_w} + x_{na} \frac{\partial \rho}{\partial x_{na}} \right] \right\} + \ln P_{H_2O}^\infty \quad (3.27) \\
\ln P_{HNO_3}^r &= \frac{2M_{HNO_3}\sigma}{RT \rho} \left\{ 1 + \frac{1}{\rho} \left[ x_w \frac{\partial \rho}{\partial x_w} + (x_{na} - 1) \frac{\partial \rho}{\partial x_{na}} \right] \right\} + \ln P_{HNO_3}^\infty \quad (3.28) \\
\ln P_{H_2SO_4}^r &= \frac{2M_{H_2SO_4}\sigma}{RT \rho} \left\{ 1 + \frac{1}{\rho} \left[ x_w \frac{\partial \rho}{\partial x_w} + x_{na} \frac{\partial \rho}{\partial x_{na}} \right] \right\} + \ln P_{H_2SO_4}^\infty \quad (3.29)
\end{align*}
\]

Note that the vapor pressure equations for $HNO_3$ and $H_2O$ are slightly different from those predicted by the general expression B.19 derived in Appendix B due to the selection of a different set of $x_i$ for the summation term. The advantage of this particular selection is that there are only four partial differentials ($\partial \rho/\partial x_w$, $\partial \rho/\partial x_{na}$, $\partial \sigma/\partial x_w$, $\partial \sigma/\partial x_{na}$) instead of six to be evaluated. In the next two sections, we shall focus on the methods used for the calculation of $\rho$ and $\sigma$, and their partial differentials with respect to $x_w$ and $x_{na}$.

### 3.2.2 Ternary Mixture Density

Due to the lack of experimental data on the density of ternary $H_2SO_4/HNO_3/H_2O$ aqueous solutions, these values have to be estimated by the use of binary density data. In principle, there are three methods of estimation based on the assumption of additivity of volume of individual components in the ternary aqueous solution. They are

1. Addition of volume of three unary, pure components.
2. Addition of volume of two binary aqueous acid mixtures.
3. Addition of volume of three binary aqueous acid mixtures.

For ideal solutions, the total volume is given by the sum of volumes of the components before mixing, i.e. the first method of volume additivity stated above can be used.
However, the ternary acid mixture considered in this study is far from ideal and more elaborate schemes are needed for the estimation of solution density. Among the above three methods, the second and third method should give a more accurate estimate of the ternary mixture density as more information is used in the calculations. It is expected that the effect of volume contraction or expansion due to mixing can at least be partially taken into account by the use of binary mixture density data. In this section, the equations for the density of $H_2SO_4/HNO_3/H_2O$ ternary mixture are derived using both the second and third method of approximation. Experimental data from the literature are used to determine the best method for this study. Binary density data are obtained from the International Critical Tables [60] and fitted with polynomial equations. The equations for the first method and two other possible combinations of the second method are given in Appendix C for reference.

To estimate the bulk density using the third method, the ternary solution is first subdivided into three binary acid solutions by mixing half of the mass of each component with each other. Illustrated in Figure 3-la is a pie chart for the distribution of weight fraction among the three binary acids. The masses of the three binary mixtures $H_2SO_4/HNO_3$ ($sn$), $H_2SO_4/H_2O$ ($sw$) and $HNO_3/H_2O$ ($nw$) can be calculated as below:

\[
M_{sn} = \frac{MT}{2} (x_{sa} + x_{na}) = MT x_{sn} \tag{3.30}
\]

\[
M_{sw} = \frac{MT}{2} (x_{sa} + x_{w}) = MT x_{sw} \tag{3.31}
\]

\[
M_{nw} = \frac{MT}{2} (x_{na} + x_{w}) = MT x_{nw} \tag{3.32}
\]

where $x_{sn}$, $x_{sw}$ and $x_{nw}$ are the weight fraction of binary mixture $H_2SO_4/HNO_3$, $H_2SO_4/H_2O$ and $HNO_3/H_2O$ respectively. Making use of the relationship $M_{ij} = \rho_{ij} V_{ij}$, where $\rho_{ij}$ and $V_{ij}$ are the density and volume of the binary mixture $ij$ and applying the assumption of volume additivity, we then have

\[
\frac{MT}{\rho} = \frac{MT}{2} \left( \frac{x_{na} + x_{sa}}{\rho_{sn}} + \frac{x_{sa} + x_{w}}{\rho_{sw}} + \frac{x_{na} + x_{w}}{\rho_{nw}} \right) \tag{3.33}
\]
Figure 3-1: Distribution of weight fraction among the corresponding binary systems: (a) Three-Binary approximation; (b) Two-Binary approximation.

or

\[ \rho = \frac{2\rho_{sn}\rho_{sw}\rho_{nw}}{(x_{na} + x_{sa})\rho_{sw}\rho_{nw} + (x_{sa} + x_{s})\rho_{sn}\rho_{nw} + (x_{na} + x_{w})\rho_{sn}\rho_{sw}} \]  

(3.34)

In the above equations, the binary mixture densities \( \rho_{sn}, \rho_{sw}, \) and \( \rho_{nw} \) should be evaluated at the equivalent binary weight fraction \( x_{b}^{s}, x_{b}^{w}, \) and \( x_{n}^{b} \) defined as:

\[ x_{b}^{s} = \frac{x_{sa}}{x_{sa} + x_{na}} \]  

(3.35)

\[ x_{b}^{w} = \frac{x_{w}}{x_{sa} + x_{w}} \]  

(3.36)

\[ x_{n}^{b} = \frac{x_{na}}{x_{na} + x_{w}} \]  

(3.37)

respectively. It should be noted that the choosing of the parameter set \( \{x_{s}^{b}, x_{w}^{b}, x_{n}^{b}\} \) is just a matter of convenience for the clarity of notation and it is by no means unique. A similar result could have been obtained had we chosen other possible parameter sets. Also there are only two independent variables (in this case, \( x_{w} \) and \( x_{na} \)) involved in the calculation as one of the weight fractions can always be found through the relationship \( \sum_{i} x_{i} = 1. \)

For the second case, there are three possible ways of choosing the two binary acid mixtures. They are:
Only the first combination is discussed in this section and equations for the other two combinations can be found in Appendix C. Similar to the third method, the ternary solution is first subdivided into the two corresponding binary acids by, in this case, combining each half of the mass of water with the mass of the two pure acids, as shown in Figure 3-1b. The masses of the two binary mixtures $H_2SO_4/H_2O$ (sw) and $HNO_3/H_2O$ (nw) are given as

\[
M_{sw} = M_T \left( x_{sa} + \frac{x_w}{2} \right) = M_T x_{sw} \tag{3.38}
\]

\[
M_{nw} = M_T \left( x_{na} + \frac{x_w}{2} \right) = M_T x_{nw} \tag{3.39}
\]

Note the difference between the above two equations and Eqs. (3.31) and (3.32). Applying again the assumption of volume additivity then gives

\[
\frac{1}{\rho} = \frac{2x_{na} + x_w}{2\rho_{nw}} + \frac{2x_{sa} + x_w}{2\rho_{sw}} \tag{3.40}
\]

or

\[
\rho = \frac{\rho_{sw}\rho_{nw}}{x_{sa}\rho_{nw} + x_{na}\rho_{sw} + \frac{x_w}{2} \left( \rho_{nw} + \rho_{sw} \right)} \tag{3.41}
\]

Similarly, the binary densities in the above equation should be calculated using the appropriate equivalent binary weight fractions. For this particular case, they are defined as follows for $\rho_{sw}$ and $\rho_{nw}$ respectively:

\[
x_{w}^b = \frac{x_w/2}{x_{sa} + x_w/2} \tag{3.42}
\]

\[
x_{n}^b = \frac{x_{na}}{x_{na} + x_w/2} \tag{3.43}
\]

Later in this section, we will compare both Eqs. (3.34) and (3.41) with the measured values of ternary density in the literature in order to select the most appropriate
Table 3.1: Partial differentials for the Three-Binary mixtures approximation.

<table>
<thead>
<tr>
<th></th>
<th>( x_b^n )</th>
<th>( x_b^w )</th>
<th>( x_b^n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{\partial}{\partial x_w} )</td>
<td>(-x_{na})</td>
<td>(1)</td>
<td>(-x_{na})</td>
</tr>
<tr>
<td>( \frac{\partial}{\partial x_{na}} )</td>
<td>(-1)</td>
<td>(x_w)</td>
<td>(x_w)</td>
</tr>
</tbody>
</table>

\[
\text{Table 3.1: Partial differentials for the Three-Binary mixtures approximation.}
\]

equation for \( p \).

As has been shown in the last section, both \( \partial p/\partial x_w \) and \( \partial p/\partial x_{na} \) are required for the calculation of the vapor pressures of ternary microdroplets. The rest of this section is therefore devoted to the evaluation of these two quantities. To begin with, we differentiate Eq. (3.33) for the Three-Binary mixtures model with respect to \( x_w \) as follows,

\[
\frac{\partial (1/p)}{\partial x_w} = \frac{1}{2} \left\{ \frac{1}{\rho_{nw}} - \frac{(x_{na}+x_w)}{\rho_{nw}^2} \frac{\partial x_n^b}{\partial x_w} - \frac{(1-x_{na})}{\rho_{sn}^2} \frac{\partial x_n^b}{\partial x_w} - \frac{(1-x_{na})}{\rho_{sw}^2} \frac{\partial x_n^b}{\partial x_w} - \frac{x_{na}}{\rho_{sn}^2 (1-x_w)} \frac{\partial \rho_{sn}}{\partial x_w} \right\} \tag{3.44}
\]

where \( \frac{\partial x_n^b}{\partial x_w}, \frac{\partial x_n^b}{\partial x_w}, \) and \( \frac{\partial x_n^b}{\partial x_w}, \) listed in Table 3.1, are calculated using Eqs. (3.35) - (3.37).

Utilizing the differential relationship

\[
\frac{\partial \rho}{\partial x_w} = -\rho^2 \frac{\partial (1/p)}{\partial x_w} \tag{3.45}
\]

we then have

\[
\frac{\partial \rho}{\partial x_w} = -\frac{\rho^2}{2} \left[ \frac{1}{\rho_{nw}} + \frac{x_{na}}{\rho_{nw}^2 (x_{na} + x_w)} \frac{d \rho_{nw}}{d x_n^b} - \frac{1}{\rho_{sw}^2} \frac{d \rho_{sw}}{d x_n^b} - \frac{1}{\rho_{sn}^2 (1-x_w)} \frac{d \rho_{sn}}{d x_n^b} \right] \tag{3.46}
\]

Similarly, differentiating Eq. (3.33) with respect to \( x_{na} \) gives

\[
\frac{\partial \rho}{\partial x_{na}} = -\frac{\rho^2}{2} \left[ \frac{1}{\rho_{nw}} - \frac{x_w}{\rho_{nw}^2 (x_{na} + x_w)} \frac{d \rho_{nw}}{d x_n^b} - \frac{1}{\rho_{sw}^2 (1-x_{na})} \frac{d \rho_{sw}}{d x_n^b} + \frac{1}{\rho_{sn}^2} \frac{d \rho_{sn}}{d x_n^b} \right] \tag{3.47}
\]

Eqs. (3.46) and (3.47) make it possible for us to estimate the value of \( \partial \rho/\partial x_w \) and \( \partial \rho/\partial x_{na} \) at a particular composition \( \{x_w, x_{na}\} \) using only binary density data.
<table>
<thead>
<tr>
<th></th>
<th>$x^b_s$</th>
<th>$x^b_w$</th>
<th>$x^b_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{\partial}{\partial x_w}$</td>
<td>$\frac{2(1-x_{na}-x_w/2)}{x_{nw}}$</td>
<td>$\frac{2(1-x_{na}-x_w/2)}{x_{nw}}$</td>
<td>$\frac{2(1-x_{na}+x_w/2)}{x_{nw}}$</td>
</tr>
<tr>
<td>$\frac{\partial}{\partial x_{na}}$</td>
<td>$\frac{2(1-x_{na}-x_w/2)}{x_{nw}}$</td>
<td>$\frac{2(1-x_{na}-x_w/2)}{x_{nw}}$</td>
<td>$\frac{2(1-x_{na}+x_w/2)}{x_{nw}}$</td>
</tr>
</tbody>
</table>

Table 3.2: Partial differentials for the Two-Binary mixtures approximation.

For the Two-Binary mixture model, similar equations can be obtained by partial differentiating Eq. (3.41) with respect to $x_w$ and $x_{na}$ as follows:

\[
\frac{\partial 1/\rho}{\partial x_w} = \frac{1}{2} \left[ \frac{1}{\rho_{nw}} - \frac{2(x_{na} + x_w)}{\rho^2_{nw} d^b_{x_w} \partial x_w} - \frac{1}{\rho_{sw}} - \frac{1}{\rho^2_{sw} d^b_{x_w} \partial x_w} \right]
\]

(3.48)

\[
\frac{\partial 1/\rho}{\partial x_{na}} = \frac{1}{\rho_{nw}} - \frac{(x_{na} + x_w/2)}{\rho^2_{nw} d^b_{x_n} \partial x_{na}} - \frac{1}{\rho_{sw}} - \frac{(1-x_{na} - x_w/2)}{\rho^2_{sw} d^b_{x_n} \partial x_{na}}
\]

(3.49)

Substituting the expressions of \( \partial x^b_n/\partial x_w \), \( \partial x^b_w/\partial x_w \), \( \partial x^b_n/\partial x_{na} \) and \( \partial x^b_w/\partial x_{na} \) tabulated in Table 3.2 into the above two equations and applying again Eq. (3.45), we have

\[
\frac{\partial \rho}{\partial x_w} = -\rho^2 \left[ \frac{1}{\rho_{nw}} + \frac{x_{na}}{\rho^2_{nw}(x_{na} + x_w/2) d^b_{x_n} \partial x_w} - \frac{1}{\rho_{sw}} - \frac{(1-x_{na})}{\rho^2_{sw}(1-x_{na} - x_w/2) d^b_{x_n} \partial x_w} \right]
\]

(3.50)

and

\[
\frac{\partial \rho}{\partial x_{na}} = -\rho^2 \left[ \frac{1}{\rho_{nw}} - \frac{x_w}{\rho^2_{nw}(2x_{na} + x_w) d^b_{x_n} \partial x_w} - \frac{1}{\rho_{sw}} - \frac{x_w}{\rho^2_{sw}(2-2x_{na} - x_w) d^b_{x_n} \partial x_w} \right]
\]

(3.51)

In this study, the binary densities $\rho_{sn}$, $\rho_{sw}$ and $\rho_{nw}$ are obtained by fitting data from the International Critical Tables [60] to fourth-order polynomials:

\[
\rho_{sn} = \sum_{i=0}^{4} C_i (x^b_s)^i
\]

(3.52)

\[
\rho_{sw} = \sum_{i=0}^{4} C_i (x^b_w)^i
\]

(3.53)

\[
\rho_{nw} = \sum_{i=0}^{4} C_i (x^b_n)^i
\]

(3.54)
Table 3.3: Coefficients for the binary density polynomials. (Eqs. (3.52) - (3.54)).

<table>
<thead>
<tr>
<th>Coeff.</th>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{sn}$</td>
<td>1541</td>
<td>634</td>
<td>-798</td>
<td>1436</td>
<td>-967</td>
</tr>
<tr>
<td>$\rho_{sw}$</td>
<td>1862</td>
<td>21.7</td>
<td>-4062</td>
<td>5668</td>
<td>-2507</td>
</tr>
<tr>
<td>$\rho_{nw}$</td>
<td>1004</td>
<td>459</td>
<td>918</td>
<td>-1323</td>
<td>476</td>
</tr>
</tbody>
</table>

Table 3.4: Coefficients for the differentiated binary density polynomials. Refer to Eqs. (3.55) - (3.57)

<table>
<thead>
<tr>
<th>Coeff.</th>
<th>$C'_0$</th>
<th>$C'_1$</th>
<th>$C'_2$</th>
<th>$C'_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d\rho_{sn}/dx_s^b$</td>
<td>634</td>
<td>-1596</td>
<td>4308</td>
<td>-3868</td>
</tr>
<tr>
<td>$d\rho_{sw}/dx_w^b$</td>
<td>21.7</td>
<td>-8124</td>
<td>17004</td>
<td>-10028</td>
</tr>
<tr>
<td>$d\rho_{nw}/dx_n^b$</td>
<td>459</td>
<td>1836</td>
<td>-3969</td>
<td>1904</td>
</tr>
</tbody>
</table>

The polynomial coefficients $C_i$ are given in Table 3.3. The unit for the binary densities is $Kg/m^3$ and it can be easily converted to specific gravity ($g/cc$) by a multiplication factor of $10^{-3}$. Calculating the derivatives of the binary density polynomials is straightforward. They are:

$$\frac{d\rho_{sn}}{dx_s^b} = \sum_{i=0}^{3} C'_i (x_s^b)^i$$ (3.55)

$$\frac{d\rho_{sw}}{dx_w^b} = \sum_{i=0}^{3} C'_i (x_w^b)^i$$ (3.56)

$$\frac{d\rho_{nw}}{dx_n^b} = \sum_{i=0}^{3} C'_i (x_n^b)^i$$ (3.57)

The new polynomial coefficients $C'_i$ are tabulated in Table 3.4. In the above polynomial equations, the temperature dependence of the density is neglected for simplicity. It is expected that at the temperature range of stratospheric interests, this temperature dependence is just a secondary effect comparing with the reciprocal temperature term in the Kelvin factor.

Pascal and Garnier [65] measured the density of the $H_2SO_4/HNO_3/H_2O$ ternary system at various temperatures. Their measurements, however, are insufficient to cover the whole range of composition. In this study, ternary density data (38 points)
from their measurements are used to test the reliability of the ternary density equations. In Figure 3-2, the relative percentage error of the calculated density, defined as

\[ E_r = \left( \frac{\rho_m - \rho_c}{\rho_m} \right) \times 100\% \quad (3.58) \]

where \( \rho_m \) and \( \rho_c \) are the measured and calculated ternary densities respectively, is plotted against the weight fraction of nitric acid. Each point in the plot represents a different ternary composition used by Pascal and Garnier (\( H_2SO_4: 7 - 90.1\%; \) \( HNO_3: 0 - 80\% \)).

Figure 3-2 shows that the relative percentage error is generally less than 5% for both Two-Binary mixtures and Three-Binary mixtures models while the Three-Unary mixtures model predicts unrealistically low values for \( \rho \) due to an over-estimation of the total mixture volume. It also illustrates that both Eqs. (3.34) and (3.41) tend to underestimate the ternary density as \( E_r \) is greater than zero (i.e. \( \rho_m \geq \rho_c \)) for most of the composition. Figure 3-3 and 3-4 are contour plots of the calculated ternary density using Eqs. (3.34) and (3.41) respectively. It is obvious from the two figures that both Eqs. (3.34) and (3.41) are smooth and continuous within the whole range of \( x_w \) and \( x_{na} \), and so the partial derivatives of \( \rho \) with respect to \( x_w \) and \( x_{na} \) should always be finite. In the following analysis, we select the Two-Binary mixtures model for the estimation of ternary density for its consistency with the surface tension equation derived in the next section.

### 3.2.3 Ternary Mixture Surface Tension

It has been recognized that the accuracy of surface energy is extremely important in predicting the nucleation rate of atmospheric aerosols and clouds. It is not uncommon for a small variation in surface tension to cause a dramatic change in the calculated nucleation rate. Unfortunately, there has not been any systematic study on the surface tension of aqueous ternary acid solutions. In this section, the surface tension for the ternary system \( H_2SO_4/HNO_3/H_2O \) is estimated using a simple rule of mixtures and the best available data in the literature. The same two binary mixture model
Figure 3-2: Relative percentage error $E_r$ of the calculated ternary densities as a function of weight fraction of nitric acid.
Figure 3-3: Contour plot of the calculated ternary acid density using the Three-Binary mixtures model.

Figure 3-4: Contour plot of the calculated ternary acid density using the Two-Binary mixtures model.
\( H_2SO_4/H_2O \) and \( HNO_3/H_2O \) for the calculation of ternary density in the previous section is chosen since there are insufficient surface tension data for the \( H_2SO_4/HNO_3 \) binary system.

Consider a spherical droplet of ternary system \( H_2SO_4/HNO_3/H_2O \) that has been subdivided into two binary acid mixtures as described in Figure 3-1b. The binary acid mixtures are treated as single species here so as to simplify the picture. In order to proceed with the calculation, it has to be assumed that the two acid species are well-mixed inside the droplet and there is no interaction (long-range or short-range) between them. Also assumed is the absence of any special surface aggregation effect and thermal variation within the droplet. As has been shown in the last section, this kind of simplified picture of aqueous mixtures does predict reasonable results as long as the binary mixture data are used.

With the assumptions stated above, the probability of finding a particular binary mixture species per unit area on the droplet surface is then proportional to the volume fraction of that species and hence the ternary surface tension can be roughly approximated as follows:

\[
\sigma = \sigma_{sw} V_{sw} + \sigma_{nw} V_{nw}
\]

(3.59)

where \( \sigma_{ij} \) and \( V_{ij} \) are the surface tension and volume fraction of the binary mixture \( ij \) respectively. The relationship between the volume fraction and the weight fraction of binary mixture \( ij \) can be found by first rewriting Eq. (3.41) into the following form:

\[
\rho = \frac{\rho_{sw} \rho_{nw}}{x_{sw} \rho_{nw} + x_{nw} \rho_{sw}}
\]

(3.60)

where the definitions of the weight fraction of binary mixtures, \( x_{sw} \) and \( x_{nw} \) have already been shown in Eqs. (3.38) and (3.39). Inverting Eq. (3.60) and comparing it with \( V_{sw} + V_{nw} = 1 \), we obtain the following relationship for \( V_{ij} \) and \( x_{ij} \):

\[
V_{ij} = \frac{\rho x_{ij}}{\rho_{ij}}
\]

(3.61)
Substituting Eq. (3.61) into (3.59) gives

\[ \sigma = \rho (\Sigma_{sw} + \Sigma_{nw}) \]  

(3.62)

where

\[ \Sigma_{sw} = \frac{\sigma_{sw} x_{sw}}{\rho_{sw}} \]  

(3.63)

\[ \Sigma_{nw} = \frac{\sigma_{nw} x_{nw}}{\rho_{nw}} \]  

(3.64)

The calculation of \( \rho_{sw} \) and \( \rho_{nw} \) has already been discussed in the previous section. Like \( \rho_{ij} \), \( \sigma_{ij} \) should also be calculated using the equivalent binary weight fractions, defined as

\[ x_{i}^{b} = \frac{x_{i}}{x_{i} + \frac{x_{w}}{2}} \]  

(3.65)

\[ x_{n}^{b} = \frac{x_{n}}{x_{n} + \frac{x_{w}}{2}} \]  

(3.66)

for binary sulfuric acid and nitric acid respectively.

Although Eq. (3.62) gives a fairly good estimate of the surface tension for diluted solutions, one has to be cautious when it is applied to more concentrated ternary acid solutions composed of electrolytes that exhibit multiple degrees of ionization. For instance, sulfuric acid, the main component of the ternary acid system at normal stratospheric temperatures, is known to be a mixture of three different forms of solutes: sulfate (\( SO_{4}^{2-} \)), bisulfate (\( HSO_{4}^{-} \)), and the molecular sulfuric acid (\( H_{2}SO_{4} \)). The proportions of these components depend not just on the overall molality [66], but also on the concentration of nitric acid in the mixture [67].
Chapter 4

Kinetic Phase Transition of Stratospheric Sulfate Aerosols

4.1 Introduction

Chemical reactions on heterogeneous surfaces such as SSAs and PSCs in the lower stratosphere are believed to be responsible for the catalytic destruction of polar ozone through the release of reactive chlorine and bromine species from their non-reactive reservoir forms [68]. It is therefore important to have a fair understanding of the chemical composition and physical state of these heterogeneous particles before making any attempt to model the heterogeneous reactions. Of particular interest are the conditions under which one form of particles transforms into another. To date, the transformation process that has received the most attention is the formation of Type Ia PSCs (NAT) particles on/in the background sulfate aerosols during the long dark polar winter. Recent evidence for the existence of another kind of PSCs particles (Type Ib) which possesses the properties of the liquid aerosols has further deepened the controversy.

It is the goal of this chapter to shed light on the formation mechanisms of both Type Ia and Ib PSCs. To accomplish this, the equilibrium phase diagrams of the two most important acid systems in the winter lower stratosphere, $HNO_3/H_2O$ and $H_2SO_4/HNO_3/H_2O$, are constructed using information obtained from the DSC mea-
surements. To further our understanding of the actual supercooling properties of the micron-sized aerosols, acid emulsion systems are developed and the DSC thermograms of these systems are then used to construct the kinetic phase diagrams. This kind of phase diagrams should provide information more relevant to the real situation.

In view of the many interacting factors that determine the manner in which a typical phase transition proceeds, a complete analysis of the kinetics of the process is virtually impossible. Nevertheless, with the assumption that all the acid solutions considered here have the potential to form glasses under the right conditions (e.g. rapid cooling rate, small sample size etc.), a simple kinetic model for the non-isothermal crystallization can be used in this study to describe the degree of crystallinity as a function of time. The same model is then used to estimate the relevant kinetic parameters from the DSC transition peaks.

4.2 The Glass Transition Phenomenon

Although the formation of glasses is not a commonly observed phenomenon, it does occur in very diverse classes of materials including pure elements (e.g. phosphorus, sulfur and selenium), oxides (e.g. SiO₂, B₂O₃ and P₂O₅), chalcogenides (e.g. As – S, As – Se and P – Se), halides (e.g. BeF₂, ZnCl₂ and ZrF₄), organic compounds (e.g. methanol, glycerol and toluene), polymers (e.g. polyethylene, polyvinyl chloride and polystyrene), metallic alloys (e.g. Pd–Si, Fe–B and Cu–Zn) and aqueous solutions of salts, acids and bases (e.g. H₂SO₄, KOH and LiCl). The simplest way to make glasses is by quenching of a liquid with strong glass-forming tendency. When a liquid is cooled sufficiently slowly, it usually goes to its most stable state, i.e. the crystalline state. If the same liquid is cooled fast enough to avoid crystallization, its viscosity would increase to a value comparable to that of a solid. The temperature range over which a given liquid system gradually transforms upon cooling from a supercooled liquid state into the glassy (or vitreous) state is defined as the glass transition range or \( T_g \) range. Even though most of the glasses appear to be in equilibrium with their surroundings, the truth is that they are always attempting to return to their
Figure 4-1: The volume-temperature diagram for a hypothetical glass-forming liquid.

The glass transition phenomenon is generally observed as a relaxation process when the temperature-dependent structural relaxation time of the supercooled liquid becomes much larger than the experimental time scale.[69] It is, however, easier to obtain a clearer picture of the fundamentals of glass transition by considering the volume-temperature relationship (the V-T diagram) of the glass-forming system at constant pressure. Figure 4-1 is such a diagram for a hypothetical glass-forming liquid. In the diagram, point “b” corresponds to the equilibrium melting temperature, $T_m$, at which an infinitely small amount of crystals is in thermodynamic equilibrium with the liquid.

On cooling, the volume of the liquid (initially at point “a”) gradually decreases
along the path “abc”. Ideally, the liquid should transform into crystalline phase at point “b” (temperature \( T_m \)) and hence should exhibit a discontinuity in the V-T diagram (line “bd”). However, for a perceptible level of crystallization, a certain degree of supercooling (say to point “c”) is often required. Under normal circumstances, the location of the freezing point “c” depends not just upon the intensity of the thermodynamic driving force for nucleation, but also upon the linear growth velocity of the activated crystallites. Consequently, the exact crystallization path cannot be pinpointed without first specifying the system parameters and the transition conditions such as the acid weight percentage and the cooling rate. Upon further cooling after crystallization, the crystalline phase should continue to shrink along the crystal line to point “e”. The less steeper slope of the crystal line simply reflects the smaller coefficient of thermal expansion of solid with respect to liquid.

On the other hand, if crystallization does not occur below \( T_m \) (mostly due to large cooling rate or high viscosity), the liquid simply moves into the supercooled liquid state along the line “bcf”, which is just an extrapolation of the line “abc”. As illustrated, the volume of the liquid shrinks with decreasing temperature implying that the structure of the liquid continuously rearranges itself into a smaller volume as required by a lower internal energy state. As cooling continues, the molecules in the supercooled liquid become less and less mobile due to the rapidly increasing viscosity. This behavior continues until the temperature is so low that the liquid molecules cannot rearrange themselves fast enough to attain the volume characteristic of that temperature. At this point the supercooled liquid line “bc” begins to bend slightly upward and eventually becomes a near-straight line that is often parallel to the crystal line “de”. The system is now said to be in the glassy state.

Unlike equilibrium melting, the transition so described does not occur at a single, sharp value of the temperature. The smooth curve between the supercooled liquid line and the glass line is known as the glass transition range. The fictive temperature, \( T_f \), is deduced by the intersection of the extrapolated glass line (“gi” and “hj”) and the supercooled liquid line “abcf”. As a conceptual approximation, one may regard \( T_f \) as the temperature at which the molecular structure of the supercooled liquid transforms
instantaneously into the glassy state. As mentioned before, the location of the glass transition region depends predominantly upon the rate of cooling. In general, the slower the cooling rate, the longer the time available for structure relaxation and hence the lower the fictive temperature.

4.3 Crystallization in Supercooled Acids

It has been known for over a century that inorganic acids such as sulfuric acid and nitric acid possess the distinct property to remain in the liquid state upon cooling[70]. This is especially true when the concentration of the acid is relatively high. The fact that the composition of stratospheric sulfate aerosols in the polar regions covers both the high and low concentration range of sulfuric and nitric acids has made their physical state an important subject in the current polar ozone hole studies. In this section, the fundamentals of nucleation and growth kinetics are discussed, with emphasis on the isothermal condition. The isothermal result is then modified to account for the non-isothermal effect.

4.3.1 Basic Concepts of Nucleation and Crystallization

The concepts which underlie the theoretical description of nucleation and growth were originally set forth by Volmer and Weber[71]. It was, nonetheless, Becker and Döring[72] who first recognized that supercooling is a consequence of the fact that the formation of a new phase must be accompanied by the simultaneous creation of a phase boundary. In other words, the free energy of formation of, say, a spherical particle of the new phase should be composed of two opposing energy terms:

\[
\Delta G_f = \frac{4\pi}{3} r^3 \rho \Delta \mu + 4\pi r^2 \sigma
\]  

(4.1)

where \( r \) is the radius, \( \rho \) is the average density of the solid and liquid phases, \( \Delta \mu \) is the difference in chemical potential (per unit of mass) between the solid and liquid
phases and \( \sigma \) is the surface tension at the phase boundary. The critical values of \( r \) and \( \Delta G_f \) can be easily obtained by maximizing \( \Delta G_f \) with respect to \( r \):

\[
\begin{align*}
    r^* &= -\frac{2\sigma}{\Delta \mu} \\
    \Delta G_f^* &= \frac{16\pi \sigma^3}{3\Delta \mu^2}
\end{align*}
\]  

Eqs. (4.2) and (4.3) are based on the so-called capillary assumption, viz. the values of \( \Delta \mu \) and \( \sigma \) do not depend on the radius \( r \) of the cluster. Hence, if it were experimentally possible to determine \( \Delta G_f^* \) at a temperature \( T \) (i.e. at a known value of \( \Delta \mu \)), \( \sigma \) can be calculated from Eq. (4.3) and \( r^* \) from Eq. (4.2). Complete description of the classical theory of nucleation can be found in numerous literatures [73, 74, 75, 76].

Illustrated in Figure 4-2 are the variations of the crystal growth rate and homogeneous nucleation rate with temperature for a hypothetical glass-forming system. As a general rule, the nucleation peak often occurs at a temperature lower than the crystal growth peak. Since nucleation must precede crystal growth, it is then quite obvious that the extent of the overlap between the two curves, shown in the figure as the shaded area, should determine, in general, the capability of a supercooled liquid to crystallize upon cooling, i.e. the larger the overlap, the easier the crystallization of the liquid. It has been known that for some concentrated sulfuric acid systems, crystallization can only be observed during the reheating process. This kind of behavior can be easily explained by imagining a system which has no or little overlap between its nucleation and crystal growth curves. For this particular kind of system, the supercooled liquid will most likely transform directly into solid glass during the first cooling. Crystallization will then occur at the activated nucleation sites during the reheating process.

### 4.3.2 Kinetics of Isothermal Crystallization

The mathematical formulation of the overall crystallization kinetics can be traced back to the fundamental works by Johnson and Mehl[77] and Avrami[78, 79, 80].
Figure 4-2: Variation of the crystal growth rate and nucleation rate with temperature for a hypothetical glass-forming system.
The model they considered involves mainly the nucleation and growth processes of a new phase embedded in a mother phase under strict isothermal conditions. In the case of non-isothermal transformations, it has been shown[81, 78, 82] that the equation so developed can only be applied in a limited number of special cases. They will be further discussed in the next section.

In a slightly modified way, the isothermal overall kinetics as derived by Avrami will be briefly reviewed here in order to provide an introduction to the mathematical adaptations which are required when this approach is applied to the non-isothermal conditions. The assumptions adopted here are basically the same as those in Avrami’s original work, viz.

1. **Spatially random nucleation.** In a supercooled liquid system, nuclei (either homogeneous or heterogeneous) are assumed to appear at random points throughout the liquid mass.

2. **Time-dependence of nucleation.** These nuclei may appear instantaneously at the beginning of the crystallization, once the effective temperature is reached; or they may appear in the unconverted phase progressively throughout the course of the process. In the former case the dependence of nucleation events on time is of zeroth order while first order is often assumed for the latter case.

3. **The nature of the growth process.** The growth process of the new phase is assumed to be either diffusion-controlled or interface-controlled and it can take place in one, two, or three dimensions to give rod-, disc-, or sphere-like crystallites respectively.

4. **The composition of the growing phase.** The converted crystalline phase is assumed to be free of impurities for the binary and ternary acid systems considered here.

Depending on the composition of the acid mixtures, the final frozen products may or may not be 100 percent crystalline. This is true even for bulk acid mixture samples where heterogeneous nucleation dominates.[50]. The reason that highly concentrated
acid mixtures can remain in the amorphous glassy state under extreme supercooled conditions is most likely due to their very high viscosity at low temperatures, as observed recently by Williams and Long[83]. For this kind of semi-crystalline materials, it is essential to have a simple, well-defined quantity to describe the entire process of crystallization.

The degree of crystallinity\(^1\) \(\xi_V\) is defined by Avrami as the ratio of the volume fraction \(V\) of the crystalline phase to the total volume fraction \(V_\infty\) of potentially crystallizable material. The condition \(V = V_\infty\) is assumed to be true only when crystallization time \(t \to \infty\). In order to apply Avrami's approach to our DSC results, the degree of crystallinity \(\xi_W\) is redefined here as the ratio of the weight fraction \(W\) of the crystalline phase to the total weight fraction \(W_\infty\) of potentially crystallizable material. Obviously, \(\xi_W\) is related to \(\xi_V\) in a nonlinear manner.

With this new definition of \(\xi\), we can now write down the expression for the number \(dN'\) of nuclei formed between time \(\tau\) and time \(\tau + d\tau\) assuming that crystallization is initiated by a sudden drop of temperature from above the equilibrium melting point \(T_m\) to a constant temperature \(T_c < T_m\),

\[
dN' = \dot{N}(\tau)[1 - \xi(\tau)]d\tau \tag{4.4}
\]

where \(\dot{N}(\tau)\) is the rate of nucleation in \(s^{-1}\) at the instant \(\tau\). The above equation can be used to estimate the total number of activated nuclei \(N'\) at time \(t\) after crystallization was started as long as the functionality of \(\dot{N}(\tau)\) has been specified,

\[
N'(t) = \int_0^t \dot{N}(\tau)[1 - \xi(\tau)]d\tau. \tag{4.5}
\]

The term \([1 - \xi(\tau)]\) in Eq. (4.4) and (4.5) was originally proposed by Avrami as a correction factor to account for the influence of the swallowing of potential nucleation sites by already growing crystallites of the new phase. He also assumed a fixed, temperature-independent value for the number of initially present potential nuclei.

\(^1\) Also known as the extent of crystallization.
per unit volume, $\bar{N}$, based upon the observation that nucleation of the solid phase in a supercooled melt almost exclusively occurs at the surfaces of foreign particles. At a certain degree of supercooling, it was presumed that $\bar{N}$ would be decreased by both the direct nuclei activation mechanism and the swallowing phenomenon. In the case of homogeneous nucleation, every point in the supercooled liquid phase space can be considered as a potential nucleation site due to the stochastic nature inherent in the process. Hence, the same correction factor can be used without modification. It is, however, important to point out that the influence of the correction factor has to be disregarded in order to obtain any intelligible expression for $\xi(t)$.

The final form of the overall kinetic equation can be obtained by first ignoring the overlapping of growth of the crystalline phase and then taking it into account later using a simple probability argument. Considering a single crystallite in the supercooled liquid phase with start of growth at time $\tau$, its volume $v(t, \tau)$ at a later time $t$ can be expressed as

$$v(t, \tau) = \int_{\tau}^{t} \dot{v}dt' = \Omega_m \left[ \int_{\tau}^{t} Gdt' \right]^m$$  \hspace{1cm} (4.6)

where $\dot{v}$ is the volume growth rate, $G$ is the linear growth rate and $\Omega_m$ a geometrical shape factor with value determined by the growth dimension $m$. For three-dimensional spherical growth ($m = 3$), $\Omega_m$ has the constant value of $4\pi/3$. This is, however, not the case for one- and two-dimensional growth where $\Omega_m$ depends on other dimensional parameters as well: $\Omega_1 = \pi R_o^2$ and $\Omega_2 = \pi h$, where $R_o$ and $h$ are the rod radius and the disc thickness respectively. The crystallite volume $v(t, \tau)$ is simply related to its mass $w(t, \tau)$ through

$$w(t, \tau) = \rho_v v(t, \tau) = \rho_v \Omega_m \left[ \int_{\tau}^{t} Gdt' \right]^m$$  \hspace{1cm} (4.7)

with $\rho_v$ being the density of the crystalline phase. Utilizing Eqs. (4.4) and (4.7) and letting $W$ be the total mass of the system, we can now express the "unrestricted" degree of crystallinity $\xi'(t)$ in terms of the "unrestricted" crystallite volume $v'(t, \tau)$.
as follows

\[ \xi'(t) = \frac{1}{W} \int_0^t w(t, \tau) dN' = \frac{\rho_c}{W} \int_0^t \dot{N}(\tau)[1 - \xi(\tau)]v'(t, \tau) d\tau. \quad (4.8) \]

In the above derivation, we have assumed that the crystallite sphere can grow without limit. This is, of course, unrealistic as experimental observations have already revealed that the growing crystallites often impinge upon each other because of the space filling effect. To find the relation between \( \xi'(t) \) and the actual degree of crystallinity \( \xi(t) \), we consider the growth of a live crystallite into a parent matrix composed of both supercooled liquid and other growing crystallites. If the crystallites are randomly located within the parent matrix, the probability that any specific element of mass within the instantaneous growth region of the live crystallite shall lie inside an existing crystallite is just \( \xi(t) \) and hence we have,

\[ d\xi = [1 - \xi(t)]d\xi' \quad (4.9) \]

or after integration from 0 to \( t \),

\[ \xi(t) = 1 - e^{-\xi'(t)}. \quad (4.10) \]

Combining Eqs. (4.8) and (4.10) then gives us the fundamental crystallization kinetic equation:

\[ \xi(t) = 1 - \exp \left[ -\frac{\rho_c}{W} \int_0^t \dot{N}(\tau)[1 - \xi(\tau)]v'(t, \tau) d\tau \right]. \quad (4.11) \]

Eq. (4.11) holds for both isothermal and non-isothermal conditions. It is obvious that the evaluation of the overall crystallization kinetic equation requires the knowledge of the functional forms of both \( \dot{N}(\tau) \) and \( v'(t, \tau) \). While \( \dot{N}(\tau) \) usually assumes rather simple form for most commonly encountered glass-forming systems, the functional form of \( v'(t, \tau) \) (Eq. (4.6)) has been found to be quite complex and often depends strongly upon the crystal growth mechanism such as the physical process that controls the elementary crystallization events.
Two types of growth mechanism which are commonly observed in experiments are considered here. By ignoring the heat transfer problem, the rate-limiting step is assumed to be either the diffusion process of molecules to or from the growth surface (diffusion-controlled) or the rate of attachment of such molecules to the interface, once they have arrived (interface-controlled). In the case of ice formation in binary $HNO_3/H_2O$ and $H_2SO_4/H_2O$ or ternary $H_2SO_4/HNO_3/H_2O$ supercooled solutions, we may envisage the controlling mechanism to be either the diffusion of acid molecules away from the crystal fronts or the attachment of $H_2O$ molecules to the growing ice single crystals. In the first hypothesis, if an ice crystal grew from a very small but stable nucleus to a sphere of radius $r$ in time $t$, the acid molecules that were initially at the center region of the nucleus have to diffuse at least a distance $r$ in order to make space for the ice crystal.\(^2\) The Fickian diffusion model,

$$r = \sqrt{Dt}$$  \hspace{1cm} (4.12)

where $D$ is the molecular diffusion coefficient, can be applied in this situation to relate $r$ with $t$. By analogy, the linear dimension $r_D$ of a diffusion-controlled growing crystal nucleated at time $\tau$ can be expressed as follows:

$$r_D = G_D(t - \tau)^{1/2}.$$  \hspace{1cm} (4.13)

In general, the proportionality constant $G_D$ does not necessarily equal to $\sqrt{D}$. On the other hand, if the growth process is interface-controlled, the growth rate should be linear and constant with respect to time as water molecules are always present in the immediate vicinity of the growing crystal front and the liquid-to-solid molecular jump frequency depends only on temperature. Thus

$$r_I = G_I(t - \tau)$$  \hspace{1cm} (4.14)

\(^2\)This is, in fact, an understatement because the solubility of inorganic acids such as $H_2SO_4$ and $HNO_3$ in ice single crystal, although rather small, is finite. In other words, pure ice crystal cannot remain thermodynamically stable in binary/ternary acid solutions.
for interface-controlled growth. Using Eqs. (4.6), (4.13) and (4.14), we can now write down a general expression for the growth volume as follows:

\[ v_j(t, \tau) = \Omega_m G_k^m (t - \tau)^p \]  

(4.15)

where the index \( k \) can be either \( D \) (diffusion-controlled) or \( I \) (interface-controlled). \( \Omega_m \) has the same definition as above and \( p \) is a constant uniquely specified by the growth geometry and the rate-controlling process:

\[ p = \begin{cases} 
  m & \text{for interface-controlled } (k = I), \\
  m/2 & \text{for diffusion-controlled } (k = D). 
\end{cases} \]  

(4.16)

One can further the generality of Eq. (4.15) by letting \( p \) to be any real and positive number. Also if the proportionality constant \( G_k \) is a vector quantity, then Eq. (4.15) can be rewritten in the following form for 3-dimensional crystal growth,

\[ v_j(t, \tau) = \Omega_m \hat{g}_x \hat{g}_y \hat{g}_z (t - \tau)^p \]  

(4.17)

where \( \hat{g}_x, \hat{g}_y \) and \( \hat{g}_z \) are the growth rate vectors in the \( x, y \) and \( z \) directions respectively, and \( p \) is given by Eq. (4.16) with \( m = 3 \). Substituting Eqs. (4.15) and (4.16) into the fundamental crystallization kinetic equation (Eq. (4.11)) and ignoring the correction factor \([1 - \xi]\) in the integral, we have

\[ \xi(t) = 1 - \exp \left[ -\frac{\Omega_m G_k^m \rho_c}{W} \int_0^t \dot{N}(\tau)(t - \tau)^p d\tau \right]. \]  

(4.18)

It remains now to search for a suitable expression for the rate of nucleation \( \dot{N}(\tau) \). Many attempts have been made in the past\[84, 85\] to devise this function and it has been found that the number of potential nuclei \( N(\tau) \) can be better described by a spectrum of activation times due to the irregularity of the heterogeneous surfaces,

\[ N(\tau) = \sum_{i=1}^{N} \dot{N}_i e^{-\xi_i} \]  

(4.19)
Table 4.1: Johnson-Mehl-Avrami Coefficient and its possible interpretation.

with \( \sum_{i=1}^{N} \bar{N}_i = \bar{N} \) (all \( \bar{N}_i \) being constants), and \( \zeta_i \) being the activation time of the \( i \)th activation mechanism. It is expected that \( \zeta_i \) has different temperature dependence for different activation mechanism\[86, 87, 85\].

Two limiting cases of nuclei activation, namely instantaneous nucleation and sporadic homogeneous nucleation, are first considered here. In the former case, which represents the instantaneous avalanche of nuclei on existing heterogeneities at \( \tau = 0 \), a simple \( \delta \)-function can be used to represent \( \dot{N}(\tau) \). Thus

\[
\xi(t) = 1 - \exp \left[ -\frac{\Omega_m G_k^m \rho_c \bar{N}}{W} \int_0^t \delta(\tau, 0)(t - \tau)^p d\tau \right] = 1 - \exp[-K_I t^p]. \tag{4.20}
\]

with \( K_I = \Omega_m G_k^m \rho_c \bar{N}/W \). For the case of sporadic homogeneous nucleation, \( \dot{N}(\tau) = N_0 \) is constant in time, i.e.

\[
\xi(t) = 1 - \exp \left[ -\frac{\Omega_m G_k^m \rho_c N_0}{W} \int_0^t (t - \tau)^p d\tau \right] = 1 - \exp[-K_S t^{p+1}]. \tag{4.21}
\]

where \( K_S = \Omega_m G_k^m \rho_c N_0/W(p + 1) \). Both Eqs. (4.20) and (4.21) have the form of the
so-called Johnson-Mehl-Avrami (JMA) equation:

\[ \xi(t) = 1 - \exp[-Kt^n] \]  

(4.22)

where \( K \), the crystallization rate constant, is a function of both the nucleation rate and the growth rate, and \( n \) is known as the JMA coefficient which basically depends upon the nucleation mechanism and growth morphology. The JMA equation simply describes a S-shape curve for \( \xi(t) \) which starts at \( \xi(t = 0) = 0 \) with zero initial slope, then blends upward and levels off as \( \xi(t) \to 1 \). Table 4.1 summarizes all the possible values for \( n \) calculated using Eqs. (4.16), (4.20) and (4.21) under different nucleation and growth scenarios. The range of \( n \) for the two special cases of decreasing and increasing nucleation rate for 3-dimensional growth were estimated by Avrami in his original work where he assumed an exponential functional form for the nucleation rate. In reality, \( n \) is often found to have values that are slightly different from those predicted in Table 4.1. Furthermore, for most cases, the value of \( n \) changes continuously as the transformation proceeds. This, of course, would imply a gradual change in both the nucleation rate and the growth mechanism during the crystallization process if the JMA equation holds.

One of the important implications from the above derivation is that the functional form of the transformation equation is totally independent of the growth model and nucleation mechanism. In other words, Eq. (4.22) can be used to fit any phase transformation data by simply adjusting both \( K \) and \( n \) as long as the process proceeds by simultaneous nucleation and growth of a new phase in the parent matrix and the assumptions stated at the beginning of this section are satisfied. Nevertheless, it is important to emphasize at this point that a good fit of phase transformation data using Eq. (4.22) does not necessarily means the model assumed here is valid. Results from other phase transformation experiments such as the direct measurement of nucleation and growth rate by means of optical microscopy are needed to support the proposed model. Without them, the JMA equation only provides a plausible explanation for the experimental transformation data.
A more general form of the transformation equation can be obtained with the help of Eq. (4.19), in which a spectrum of activation times is postulated. Knowing that the total number of potential nucleation sites \( N(\tau) \) and activated sites \( N'(\tau) \) at any time \( \tau \) is always equal to the number of initially present potential nuclei \( (\bar{N}) \), we can write down an alternative expression for Eq. (4.5) as follows

\[
N'(\tau) = \bar{N} - \sum_{i=1}^{N} \bar{N}_i e^{-\frac{\tau_i}{\zeta_i}} .
\]  

(4.23)

The calculation of the nucleation rate \( \dot{N}(\tau) \) is then quite straightforward,

\[
\dot{N}(\tau) = \frac{dN'}{d\tau} = \sum_{i=1}^{N} \frac{\bar{N}_i e^{-\frac{\tau}{\zeta_i}}}{\zeta_i} .
\]  

(4.24)

Substituting Eq. (4.24) into the kinetic transformation equation (Eq. (4.18)) then gives

\[
\xi(t) = 1 - \exp \left[ -\frac{\Omega_m G_k^m \rho_c}{W} \sum_{i=1}^{N} \frac{\bar{N}_i I_i(t)}{\zeta_i} \right] .
\]  

(4.25)

where

\[
I_i(t) = \int_0^t (t - \tau)^p e^{-\frac{\tau}{\zeta_i}} d\tau .
\]  

(4.26)

Assuming that \( z = t - \tau \) and hence \( dz = -d\tau \), the integral \( I_i(t) \) in the above equation can be rewritten as

\[
I_i(t) = e^{-\frac{t}{\zeta_i}} \int_0^t z^p e^{\frac{z}{\zeta_i}} dz
\]  

(4.27)

and then be evaluated using integration by parts consecutively,

\[
I_i(t) = e^{-\frac{t}{\zeta_i}} \left[ \zeta_i e^{\frac{t}{\zeta_i}} (z^p - \zeta_i p z^{p-1} + \zeta_i^2 p (p - 1) z^{p-2} - \cdots + (-1)^p \zeta_i^p p! \right]_0^t
\]  

(4.28)

with \( p > 0 \). The final form of the generalized transformation equation then reads

\[
\xi(t) = 1 - \exp \left\{ -\frac{\Omega_m G_k^m \rho_c}{W} \sum_{i=1}^{N} \bar{N}_i \left[ \sum_{j=0}^{p} \frac{(-1)^j \zeta_i^j p!}{(p - j)!} t^{p-j} - (-1)^p \zeta_i^p p! e^{-\frac{t}{\zeta_i}} \right] \right\} .
\]  

(4.29)

This equation should, in theory, describe the entire course of the isothermal crystal-
lization as long as all the kinetic parameters are known. In practice, much simpler forms of Eq. (4.29) can be used with confidence for most systems of interest.

In the case of extremely fast activation \( t \ll \zeta_i \), the exponential term and the terms up to \( t^{p-1} \) in Eq. (4.29) can be disregarded when compared with the \( t^p \) term. Eq. (4.29) then reduces to

\[
\xi(t) = 1 - \exp \left[ -\frac{\Omega_m G^m_k \rho_c}{W} \sum_{i=1}^{\mathcal{N}} \tilde{N}_i t^p \right] \tag{4.30}
\]

which is the same as Eq. (4.20) since \( \sum_{i=1}^{\mathcal{N}} \tilde{N}_i = \tilde{N} \). On the other hand, if the activation process of potential nuclei is very slow \( t \ll \zeta_i \), the first \( p+1 \) terms of the exponential series cancel against the other terms in the square bracket. Among the remaining terms, only the \( (p+1) \)th term is of significant comparing with the higher order terms, i.e.

\[
I_i(t) = \frac{(-1)^{2(p+1)}}{\zeta_i} \frac{p!}{(p+1)!} t^{p+1} = \frac{t^{p+1}}{\zeta_i(p+1)} \tag{4.31}
\]

As \( t/\zeta_i \ll 1 \), Eq. (4.24) can be approximated by the first term of the exponential series,

\[
\dot{N}(\tau) = \sum_{i=1}^{\mathcal{N}} \frac{\tilde{N}_i}{\zeta_i} \left[ 1 - \frac{\tau}{\zeta_i} + \cdots \right] \approx \sum_{i=1}^{\mathcal{N}} \frac{\tilde{N}_i}{\zeta_i} \tag{4.32}
\]

and Eq. (4.29) then becomes Eq. (4.21).

As discussed earlier in this section, the swallowing effect can account for a major fraction of loss of potential nucleation sites during the continuing growth of existing crystallites. The implication of this experimental observation is clear; only a few activation mechanisms with relatively short activation time actually determine the time-dependence of the number of potential nuclei during the simultaneous processes of nucleation and growth. In other words, the supercooled phase space can be filled with mature crystallites nucleated at an earlier stage of activation before the slower nucleation processes (with large activation times) have a chance to contribute to \( \xi(t) \).

The isothermal rate of transformation, \( d\xi/dt \), can be easily obtained by differen-
tiating Eq. (4.22) with respect to \( t \) as follows,

\[
\frac{d\xi}{dt} = Kn t^{n-1} \exp[-Kn].
\]  

(4.33)

Because of the explicit relationship between \( \xi \) and \( t \) (Eq. (4.22)), Eq. (4.33) can be rewritten in a form without \( t \),

\[
\frac{d\xi}{dt} = nK \left( 1 - \xi \right) \left[ \ln \frac{1}{(1 - \xi)} \right]^\frac{n-1}{n}.
\]  

(4.34)

Eq. (4.34) is sometimes referred to as the JMA transformation rate equation and it clearly indicates that under strict isothermal condition there is a unique relationship between the extent of crystallization, \( \xi \), and the transformation rate, \( d\xi/dt \). Note that for the particular case of \( n = 1 \), \( d\xi/dt \) at \( t = 0 \) is finite.

Beside \( K \) and \( n \), two other parameters have been suggested by various workers as an approximate measure of the overall rate of crystallization. They are induction time (\( t_i \)) and crystallization half time (\( t_\frac{1}{2} \)). The definition of \( t_i \) is based upon the observation that there is always a period at the beginning of the transformation process when the change in \( \xi(t) \) is too small to be detectable. Consequently, \( t_i \) varies widely with the method of detection. For the sake of convenience, \( \xi(t_i) \) is most often assumed to be 0.01.

Unlike \( t_i \), \( t_\frac{1}{2} \) is defined as the time required for the crystallization of half of the supercooled liquid (i.e. \( \xi(t_\frac{1}{2}) = 1/2 \)) and hence should be independent of the method of measurement. It can be readily shown from Eq. (4.22) that

\[
t_{\frac{1}{2}} = \left( \ln \frac{2}{K} \right) \frac{1}{n}.
\]  

(4.35)

Unfortunately, \( t_\frac{1}{2} \) is a combined function of \( K \) and \( n \), and hence not an unambiguous means for comparing the rates of two different processes if \( n \) is changing during the course of transformation. The reciprocal value of \( t_\frac{1}{2} \) is sometimes called the overall crystallization rate.
4.3.3 Kinetics of Non-isothermal Crystallization

The kinetic model described in the last section has been very successful in explaining isothermal transformation data. It is therefore quite natural as a first attempt to apply the very same equation to non-isothermal situations. Many attempts[88, 89, 90, 91] have been made in the past to apply Eq. (4.22) to non-isothermal conditions without any major modification. It has been found that for some particular polymeric systems at a slow enough constant cooling rate[92], Eq. (4.22) can be successfully approximated by

\[ \xi(s) = 1 - \exp\left[-K^*s^n\right] \]  

(4.36)

where \( K^* \) is constant with respect to the reduced time \( s \). This kind of transformation, where the nucleation rate is usually proportional to the growth rate, was termed isokinetic by Avrami[78]. Eq. (4.36) simply implies that a plot of \( \ln[-\ln(1 - \xi(t))] \) against \( \ln t \) should be a straight line with a slope of \( n \), whether the transformation process is isothermal or not. Nevertheless, one still has to bear in mind that the success of Eq. (4.36) depends predominantly on the system studied.

Another special case of great significance was pointed out by Cahn[82]. When all nucleation events take place early in a transformation, it is said to have undergone site saturation. There are several situations where one might expect this condition to be satisfied. In this case as long as the growth rate is dependent only on the temperature, the course of transformation will be similar at all temperatures. The only quantity that would have been affected is the rate of transformation. As one can see immediately, the transformation rate for the above two special cases is always a unique function of \( \xi \) and \( T \), and hence the application of Eq. (4.34) is justified for both isothermal and non-isothermal transformation conditions.

The fact that Eq. (4.34) cannot be applied to any non-isothermal transformations involving simultaneous nucleation and growth can be clearly illustrated by the following thought experiment. Consider the crystallization of two identical binary acid systems (e.g. \( H_2SO_4/H_2O \)) by homogeneous nucleation and growth. Suppose that acid system 1 is severely supercooled to temperature \( T_1 \) where \( T_1 \ll T_m \), the equi-
librium melting temperature of the binary acid system. After annealing for a certain period of time at $T_1$, a fraction of the supercooled liquid ($\xi_0$) would have transformed into solid crystallites. Under such condition, one can safely assume a high nucleation rate and a slow growth rate for the crystallites. Phrased somewhat differently, one should expect the crystalline phase be characterized by numerous tiny crystallites embedding in the supercooled liquid phase.

On the other hand, let acid system 2 be only slightly supercooled to temperature $T_2$ until the same fraction $\xi_0$ of crystallites have formed. By the same reasoning, the transformed phase of acid system 2 should be characterized by a relatively larger average crystal size and a smaller number of crystallites. Now if both acid systems 1 and 2 are brought to a common temperature $T_c$ with $T_c < \min\{T_1, T_2\}$, and allowed to continue the isothermal transformation process at $T_c$, we will certainly expect acid system 1 to have a much higher transformation rate than system 2 due to the larger surface area to volume ratio of the smaller size crystallites while Eq. (4.34) will erroneously predict the same transformation rates for both systems. This example clearly demonstrates the important role of thermal history, besides $\xi(t)$ and $T$, in determining the instantaneous transformation rate.

**Non-isothermal JMA Transformation Equation**

In order to apply the JMA equation to non-isothermal condition, it is essential to have a thorough understanding of the temperature dependence of the crystallization rate constant $K$. This is, nonetheless, not an easy task for systems that exhibit simultaneous nucleation and growth. Experimental studies of glass-forming systems in the past have clearly shown that a temperature jump (either positive or negative) can have an uniform effect on the overall rate of isothermal crystallization. As the number of growing nuclei is always changing during the process, the observed constancy of $K$ can only be explained by the assumption of a single rate-controlling process such as the growth rate of activated nuclei.

Fortunately, for systems that have a strong glass forming tendency the situation can be somewhat simplified due to their strong supercooling capability. As discussed
before, for this kind of systems crystallization often occurs at large degree of supercooling where the rate limiting step for growth is simply the diffusion of molecules within the liquid phase. However, at such low temperature the activation energy for diffusion can be extremely high and hence the frequency of intermolecular jump and not the rate of nucleation should be the parameter that actually controls the overall rate of crystallization. For this kind of systems, $K$ can be expressed in the simple Vogel-Fulcher form [93],

$$K = K_o \exp \left[ \frac{-\Delta H}{k(T - T_o)} \right]$$ (4.37)

where $K_o$ is the pre-exponential factor, $\Delta H$ is the appropriate activation energy, $k$ is Boltzmann’s constant and $T_o$ a constant that has the dimension of temperature. The factor $K_o$ can be assumed to be constant with respect to temperature for most glass forming systems as it is generally believed that its weak temperature dependence can be safely ignored when compared with the exponential term [93, 94].

Under the assumption of the simplified function for $K$ (Eq. (4.37)), the crucial parameters needed for the characterization of crystallization kinetics have increased to four: $\Delta H, n, T_o$ and $K_o$. If the cooling is sufficiently slow such that the extent of crystallization of the sample has enough time to relax to its isothermal value, the non-isothermal crystallization kinetics can be approximately described by combining Eqs. (4.22) and (4.37), i.e.

$$\phi = n \ln \left( \frac{T_i - T}{T} \right) - \frac{\Delta H}{k(T - T_o)} + \ln K_o$$ (4.38)

where $\phi = \ln[-\ln(1 - \xi)]$ and $T_i$ is the temperature at which crystallization begins. By assuming a value for $n$, Eq. (4.38) can then be used to describe the kinetics of crystallization of emulsified acid systems.
4.4 Experimental Techniques

4.4.1 Differential Scanning Calorimetry

Differential Scanning Calorimetry (DSC) has been widely used for the characterization of both isothermal and non-isothermal crystallization behavior of a wide range of materials. The unique feature of this particular technique is that the temperature scan rate ($\dot{T}$) of the sample can be controlled with extremely high accuracy. If the size of the sample is small enough and good thermal contact is maintained between the sample and the sample pan throughout the experiment, then for sufficiently small value of $\dot{T}$, the thermal behavior of the system can be used to accurately determine the transformation kinetics of the sample.

The Perkin-Elmer DSC-7 used in this study adopts the power compensated null-balance principle (temperature precision $\pm 0.1 \, ^\circ C$) to make sure both the sample and the reference cells have the same predetermined rate of temperature increase (or decrease). In general, the technique involves the monitoring of the difference between the electric power supplied to heat the sample cell and the power supplied to heat the reference cell, so that the temperature difference between the cells remains zero [95, 96]. The maximum sensitivity of the DSC-7 is around $0.1 \text{ meals}^{-1}$ for a full scale deflection. It requires normally only a few milligrams of sample for each measurement. The operational temperature range is from -175 to $725 \, ^\circ C$. To ensure consistent accuracy of temperature measurement, the transition temperatures (recorded during the heating scan) of n-dodecane (Purified Grade, Fisher Scientific, melting temperature = $-9.65 \, ^\circ C$) and cyclohexane GR (EM Science, solid-solid transition at $-87.06 \, ^\circ C$) were used for the calibration of temperature for both the cooling and heating experiments. Recent studies [97, 98] using high-purity liquid crystals such as $99.9\% \, (+) - 4 - n - \text{hexyloxophenyl} - 4' - (2' - \text{methylbutyl}) - \text{biphenyl} - 4 - \text{carboxylate}$ and $\, (+) - 4 - (2' - \text{methylbutyl})\text{phenyl} - 4' - n - \text{octylbiphenyl} - 4 - \text{carboxylate}$ have shown that if the heating or cooling rate does not exceed $20 \, ^\circ C/min$, the standard deviation of the accuracy of the calibration is only ca. $\pm 0.3 \, ^\circ C$.

Indium ($99.99\%, \Delta H = 28.48 \, J/g, m.p. 156.60 \, ^\circ C$) was selected as the calibration
standard for the heat of transition (see Figure 4-3) mainly because of its excellent reproducibility and well-known literature value of $\Delta H$. The maximum deviation of $\Delta H$ measured using the DSC-7 was found to be less than 0.1%. Both the sample and reference cell compartments were purged with helium gas to prevent any unwanted condensation at very low temperatures.

Two kinds of sample pan were used in this experiment, depending on the volatility of the samples. It was found that for relatively low concentration of sulfuric acid (e.g. 5 wt%), an open platinum sample pan with a thin cover was required to prevent any condensation of acid vapor on the inner side wall of the pan during a warming event. Otherwise, the condensate on the side wall would give an unwanted signal at a higher temperature probably due to the small temperature gradient of the sample pan. For other sample compositions including the emulsion systems, it was possible to use a volatile capsule pan (also made of platinum) which has the distinct advantage of retaining almost all the sample throughout the experiment. Comparison of the sample weight before and after the experiment has justified this claim. The maximum weight loss has been found to be around 1 wt%.

To estimate the extent of crystallization, one can integrate directly the DSC exothermic peak obtained during a cooling scan. Normally, the entire transition process lasts about 6 to 7 minutes for the emulsion samples, depending on the sample size, the cooling rate and, of course, the weight fraction of the acid. It is important to
point out that the sensitivity of the signals (i.e. the area under the peaks) is directly proportional to the temperature scan rate since the abscissa of the thermogram is expressed in the temperature scale. Figure 4-4 shows the DSC thermogram of a ternary acid emulsion sample with 5 wt% HNO$_3$ and 1 wt% H$_2$SO$_4$ taken with a constant cooling scan rate of -1 °C/min. The starting temperature $T_i$ ($t = 0$) is chosen arbitrarily. The deviation of the curve from the baseline at some particular temperature $T$ ($t = t'$) is simply a measure of the heat flow from the sample per unit time, i.e. $dH/dt$. As a first approximation, one can apply the Borchard assumption [99, 100]

$$\frac{dH}{dt} \propto \frac{d\xi}{dt}$$

\hspace{1cm} (4.39)
such that the area above the curve and under the baseline from time $t = 0$ to $t = t'$ (the shaded region in Figure 4-4) is roughly proportional to $\xi(t')$. The constant of proportionality for Eq. (4.39) can be determined from the normalization condition

\[
\int_0^\infty \frac{d\xi}{dt} dt = 1. \quad (4.40)
\]

### 4.4.2 Sample Preparation

Bulk acid mixtures were prepared by carefully diluting 95.6 wt% sulfuric acid and 67 wt% nitric acid (Mallinckrodt, Analytical Grade) with the appropriate amount of deionized water. The accuracy of this method was previously estimated to be around $\pm 0.1$ wt% [101, 41]. The typical volume of a bulk sample $^3$ is about 2 - 5 $\mu$l (unless stated otherwise).

The emulsion samples used in this study were made by mixing the appropriate amount of acid solutions with an oil phase containing approximately 80 wt% Halocarbon oil series 0.8 $^4$ (Halocarbon Products Corporation) and 20 wt% lanolin (Aldrich Chemical). The weight fraction of the dispersed aqueous phase in the emulsions is $\sim 0.1$ for all the samples. In order to produce a signal comparable to that of the bulk samples, approximately 20 $\pm$ 3 $\mu$l of the emulsion samples was used for each DSC measurement.

Emulsification was carried out by first shaking the volumetric flasks containing the acid-in-oil mixtures (A/O) with hands and then by a high speed mixer (Thermolyne Maxi-Mix III, Type 65800) for about 1 minute at room temperature. Under normal conditions (i.e. room temperature and atmospheric pressure), the emulsions would separate into two layers a few days after the preparation due to the difference in density of the oil and the aqueous phase ($\rho_{\text{oil}} \approx 1.7 \text{ g/cm}^3$ and $\rho_{\text{acid}} < 1.4 \text{ g/cm}^3$).

---

$^3$Note that the bulk samples defined here are considerably smaller than those used in other supercooling studies [24, 25].

$^4$Halocarbon oil series 0.8 is a blend of completely halogenated chlorotrifluoroethylene oils and is completely inert to all acids, alkalis and oxidizing agents.
4.5 Results and Discussion

4.5.1 Crystallization of Bulk Acid Systems

The primary goal of this section is to establish the identity of the solid hydrates formed by freezing ternary $H_2SO_4/HNO_3/H_2O$ bulk solutions with composition similar to the acid aerosols in the winter polar stratosphere. Classical ternary phase diagram has been found to be quite useful for this purpose. As has been suggested by the recent supercooling study of Koop et al. [25], binary $HNO_3/H_2O$ system may play a much more important role in the phase transition of stratospheric aerosols than binary $H_2SO_4/H_2O$ system even when the size effect is not taken into account. With this particular point in mind, we shall begin this section with a quick revisit of the binary $HNO_3/H_2O$ bulk system, followed by the more relevant ternary $H_2SO_4/HNO_3/H_2O$ system. Similar study on the binary $HNO_3/H_2O$ bulk system has also been carried out by Ji and Petit [102, 103].

Nitric acid solutions with composition ranging from 0 to 70.4 wt% were studied for their freezing and melting behavior. Approximately 3 μl of the acid samples was used for each measurement. The acid solutions were first cooled down to -140 °C at a cooling rate of -10 °C/min and then heated back up to the loading temperature of the samples (5 °C) at 3 °C/min. Other cooling and heating rates had also been tried and it was found that the chosen pair of rates represents the optimum combination. Other factors such as sample geometry and location were kept as constant as possible for all the DSC measurements.

Shown in Figure 4-5 to 4-13 are the DSC heating thermograms of the binary nitric acid solutions. With the exception of the 41.9 and 53.8 wt% nitric acid samples, all thermograms show an exothermic peak at temperature somewhere between -90 to -110 °C, indicating the transition of a metastable phase (probably supercooled nitric acid solution) to phases that are thermodynamically more stable (ice and NAT in this case). The glass transition temperature ($T_g$) was measured by quenching the acid samples with the highest possible cooling rate of the DSC (-150 °C/min) and was found to be around -120 °C for the bulk acid samples. As will be shown in the
Figure 4-5: DSC thermogram of 7.92 wt% nitric acid bulk system.

Figure 4-6: DSC thermogram of 20.1 wt% nitric acid bulk system.

Figure 4-7: DSC thermogram of 33.5 wt% nitric acid bulk system.
Figure 4-8: DSC thermogram of 41.9 wt% nitric acid bulk system.

Figure 4-9: DSC thermogram of 53.8 wt% nitric acid bulk system.

Figure 4-10: DSC thermogram of 58.5 wt% nitric acid bulk system.
Figure 4-11: DSC thermogram of 63.6 wt% nitric acid bulk system.

Figure 4-12: DSC thermogram of 67.0 wt% nitric acid bulk system.

Figure 4-13: DSC thermogram of 70.4 wt% nitric acid bulk system.
next section, $T_s$ is in fact a function of the nitric acid concentration. It appears that the variation can only be observed when a large fraction of the nitric acid solution sample remains in the supercooled liquid state down to $T_s$. Such a large degree of supercooling can only be achieved by the use of a very high cooling rate (quenching) or an ultra clean solution sample (emulsion).

The most distinct feature of the eutectic transition is that it always occurs at the same temperature regardless of the solution composition. This temperature ($T_e$) also happens to be the lowest temperature on the liquidus. It can be seen from the thermograms in Figure 4-5 to 4-13 that the transition peak at -43 °C possesses both of these two features. Hence, one can conclude that no nitric acid solution (0 - 70 wt%) can be present below -43 °C if the whole system is in thermodynamic equilibrium. The eutectic composition was found to be around 33.5 wt% as indicated by the absence of the final melting peak at $T > T_e$ in Figure 4-7. Also the size of the eutectic peak is at its maximum at this composition. Consequently, for acid composition greater than 33.5 wt% (the ice/NAT eutectic composition), NAT, instead of ice, should be the last solid to melt during heating. However, it is not sure from this experiment if the reverse process is true.

Nitric acid dihydrate (NAD) has also been recognized as a potential candidate of Type Ia PSCs [102, 104, 105]. NAD, with a composition of 63.6 wt% $HNO_3$, is known to be metastable when compared with NAT. Laboratory experiments have clearly demonstrated the metastability of NAD under typical stratospheric conditions [105]. But that does not mean it cannot exist in the winter lower stratosphere. The transformation of NAD to NAT occurs at a temperature approximately two degrees higher than $T_e$, as shown in Figure 4-11 to 4-13. The DSC results obtained in this experiment are in good agreement with those of Petit et al. [102, 104] As a general observation, ice, NAT and NAD seem to be the only plausible frozen products for binary $HNO_3/H_2O$ systems with acid weight percentage less than 63.6%. The temperature-composition phase diagram of this system will be discussed in the next section.

The variation of the aerosol composition with temperature under typical strato-
Table 4.2: Equilibrium composition and temperatures of ternary $H_2SO_4/HNO_3/H_2O$ solution samples calculated for the stratospheric condition of 5 ppmv $H_2O$ and 10 ppbv $HNO_3$ at 100 mbar.

spheric conditions has already been discussed in detail in Chapter 2. As illustrated in Figure 2-17, only a small section of the ternary phase diagram is of relevance to the winter lower stratosphere. That means it is not necessary for us to map out the whole ternary phase diagram in order to understand the identity of the frozen aerosols. The freezing and melting behavior of a typical ternary aerosol system along the deliquescence\textsuperscript{5} curve can be used to represent the general behavior of the whole region.

The following stratospheric condition is chosen in this study as an example: 5 ppmv $H_2O$ and 10 ppbv $HNO_3$ at 100 mbar level. The composition of the ternary aerosols calculated using the above condition can be found in Table 4.2. Generally speaking, four variables are required to fully characterize a ternary system. They are the temperature ($T$), the pressure ($P$), and two composition variables ($x$ and $y$ in this case). For condensed systems, it is possible to fix the value of $P$ so as to simplify the interpretation. It is also quite common for ternary systems in which the three components have the same relative importance to employ an equilateral triangle to

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
Sample & $x$ & $y$ & Equilibrium Temp. ($K$) \\
\hline
1 & 51.50 & 0 & 193.6 \\
2 & 49.30 & 1.05 & 193.7 \\
3 & 44.33 & 4.12 & 193.8 \\
4 & 39.45 & 7.63 & 194.0 \\
5 & 35.62 & 10.76 & 194.2 \\
6 & 32.21 & 13.79 & 194.4 \\
7 & 30.62 & 15.29 & 194.5 \\
8 & 29.09 & 16.77 & 194.6 \\
9 & 27.62 & 18.23 & 194.7 \\
10 & 26.21 & 19.65 & 194.8 \\
11 & 24.87 & 21.04 & 194.9 \\
12 & 23.59 & 22.39 & 195.0 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{5}Refer to Page 26 for the definition of “deliquescence” in this study.
represent the composition phase space, as illustrated in Figure 4-26. Such a triangular representation has the property that the sum of the three perpendiculars from any interior point to the three sides is equal to the height of the triangle and hence it can be normalized easily to represent the composition of the ternary mixture.

Two cooling procedures were employed in this study:

1. Acid samples were first rapidly cooled down to -140 °C (-50 to -150 °C/min) and then heated up to 5 °C with a rate of 2 °C/min.

2. Acid samples were cooled at a relatively slower rate (-2 to -5 °C/min) to -79 °C (194.15 K) and then heated up to 5 °C with a rate of 2 °C/min.

While the first procedure can give the true equilibrium phase characteristics of the ternary acid system, it is the second cooling procedure that is more relevant to what actually happens in the polar stratosphere before the formation of Type II PSCs near the ice frost point. In order to enhance the resolution of the transition peaks near the ternary eutectic point, a much smaller sample size (0.3 to 0.5 µl) was used. Each sample was run at least three times to ensure the reproducibility of the results.

The DSC heating thermograms of the ternary acid samples described above are reproduced in Figure 4-14 to 4-25. The first cooling procedure was adopted in this case. Figure 4-27 represents the cross-section of the ternary \( H_2SO_4/HNO_3/H_2O \) phase diagram along the trajectory described by the black dots in Figure 4-26 (also see Table 4.2). The DSC thermograms show a series of endothermic transitions at temperatures between -80 and -70 °C. One of those transition peaks (most likely the one with the lowest temperature) obviously represents the ternary eutectic transition of ice/NAT/SAT (or Sulfuric Acid Hemihexahydrate, SAH). The exothermic peaks near -73 °C (200 K) represent either the crystallization of SAH from the melt or the solid-solid transition of sulfuric acid octahydrate into SAH, as suggested by comparing these peaks with those of the binary \( H_2SO_4/H_2O \) system.

It is also shown in Figure 4-27 that the binary eutectic temperatures of ice/NAT and NAT/SAT change rapidly with the amount of \( HNO_3 \) and \( H_2SO_4 \) in the samples and they finally reach the same minimum near 29 wt% \( HNO_3 \) and 16.8 wt% \( H_2SO_4 \).
Figure 4-14: DSC heating thermogram of bulk ternary acid sample 1 (refer to Table 4.2 for the acid composition).

Figure 4-15: DSC heating thermogram of bulk ternary acid sample 2 (refer to Table 4.2 for the acid composition).

Figure 4-16: DSC heating thermogram of bulk ternary acid sample 3 (refer to Table 4.2 for the acid composition).
Figure 4-17: DSC heating thermogram of bulk ternary acid sample 4 (refer to Table 4.2 for the acid composition).

Figure 4-18: DSC heating thermogram of bulk ternary acid sample 5 (refer to Table 4.2 for the acid composition).

Figure 4-19: DSC heating thermogram of bulk ternary acid sample 6 (refer to Table 4.2 for the acid composition).
Figure 4-20: DSC heating thermogram of bulk ternary acid sample 7 (refer to Table 4.2 for the acid composition).

Figure 4-21: DSC heating thermogram of bulk ternary acid sample 8 (refer to Table 4.2 for the acid composition).

Figure 4-22: DSC heating thermogram of bulk ternary acid sample 9 (refer to Table 4.2 for the acid composition).
Figure 4-23: DSC heating thermogram of bulk ternary acid sample 10 (refer to Table 4.2 for the acid composition).

Figure 4-24: DSC heating thermogram of bulk ternary acid sample 11 (refer to Table 4.2 for the acid composition).

Figure 4-25: DSC heating thermogram of bulk ternary acid sample 12 (refer to Table 4.2 for the acid composition).
Figure 4-26: Trajectory of the sample compositions (as listed in Table 4.2) in the ternary phase diagram. Also shown are the binary eutectic lines measured by Carpenter and Lehrman.

Figure 4-27: Cross-section of the ternary phase diagram along the composition trajectory shown in Figure 4-26.
\( T_{eq} = 194.6 \, K \). Also observed is the fact that not all the binary eutectic peaks are visible due to the extremely small amount of ice/NAT and NAT/SAT eutectic mixture formed in some samples and the possible overlapping of the binary and ternary eutectic peaks. Finally, it is quite obvious from Figure 4-26 and 4-27 that there are at least three distinct stages of transition. They are marked in the ternary phase diagram as \( a \) (NAT Melting 1), \( b \) (Binary Eutectic 1) and \( c \) (Ternary Eutectic 1).

Sample 3 (44.33 \% \( HNO_3 \) and 4.12 \% \( H_2SO_4 \)) is singled out here as an example to depict the possible equilibrium freezing path of a ternary acid sample. Consider first the cooling of the acid sample starting at a temperature a few degrees above the liquidus. As the temperature of the acid sample is lowered, NAT begins to freeze out from the acid solution at point \( a \). This process continues until the binary eutectic temperature of ice/NAT is reached (point \( b \)). The composition of the acid mixture during the freezing-out of NAT can be estimated by drawing a straight line through the pure NAT point and the sample composition (line \( Nab \) in Figure 4-26). At the binary eutectic point \( b \), ice/NAT eutectic mixture begins to form in the remaining liquid. The composition of the liquid follows closely the binary eutectic line \( bc \). Meanwhile, the amount of NAT in the ice/NAT eutectic mixture gradually decreases since less and less \( HNO_3 \) molecules are available in the liquid phase. Finally, all the remaining liquid freezes into a ternary eutectic mixture of ice, NAT and sulfuric acid hydrates at a temperature close to \(-77 \, ^\circ C\) (point \( c \)). The exact composition and formation temperature of this ternary eutectic mixture cannot be accurately determined in this experiment due to the presence of other transition peaks at temperatures very close to \(-77 \, ^\circ C\).

By studying the freezing properties of bulk ternary acid solutions (\( \sim 1 \, cm^3 \)), Koop et al. [25] observed that ice was the only potential nucleus in their experimental setup that could induce nucleation of acid hydrates. They then concluded that the aerosol droplets in the lower stratosphere must be first cooled below the ice frost point before the possible formation of any acid hydrates. Their observation does not agree with the results of other freezing studies using similar bulk ternary acid solutions [40, 23] where
NAT was often one of the many frozen products formed. With all this information in mind, the question that we would like to ask is therefore whether NAT can be formed in the ternary acid solutions without the presence of ice.

The DSC heating thermograms of bulk ternary acid samples 5 and 6 obtained with the two experimental procedures described on page 122 are shown in Figure 4-28 and 4-29 respectively. It is obvious from the two figures that without going down below \(-79 \, ^\circ C \, (\sim 194 \, K)\), NAT seems to be the only solid formed in the acid solutions as indicated by the disappearing of both the binary and ternary eutectic peaks. Since the sample compartment was purged with dry helium gas throughout the experiment, the chance of any condensation of ice frost on the side wall of the sample pan was greatly
minimized. The melting temperature of NAT formed using the second experimental procedure \((T_L = -79 \, ^\circ C)\) is also plotted in Figure 4-27 (NAT Melting 2). It can be seen that the data are in good agreement with those obtained using the first procedure (NAT melting 1).

The first systematic study of the freezing temperature of \(HNO_3/H_2O\) binary system was performed by Pickering [106] at the end of the last century. Based on earlier works, Pickering had successfully identified three eutectic points and isolated two hydrate crystals of nitric acid (the mono- and trihydrate). Kuster and Kremann [107] later extended Pickering’s results to cover the whole range of the system, from pure water to pure nitric acid. More recently, Clavelin and Mirabel [42] reviewed all the vapor pressure data of this system measured near room temperature and summarized them into a new set of equations of state.

The possibility of the existence of nitric acid trihydrate (NAT) particles as the Type Ia PSCs in the lower stratosphere during polar winter was proposed independently by Crutzen and Arnold [43], McElroy et al. [10] and Toon et al. [44]. Recent low temperature vapor pressure data obtained by Hanson and Mauersberger [13, 108, 14] and theoretical analysis by Smith and Worsnop et al. [109, 105] subsequently confirmed their speculation that NAT is the most thermodynamically stable form of nitric acid hydrates under typical stratospheric conditions during polar winter. Together with evidence gathered from field measurements [15, 16] in the late 1980’s, the so-called 3-stage concept of Type I PSC formation [110, 111, 112] was postulated to explain the presence of solid cloud particles at temperatures several degrees above the ice frost point. Briefly, the 3-stage formation mechanism involves the initial freezing of the background sulfate aerosols at \(T \approx 195 \, K\) and subsequent deposition of \(HNO_3\) and \(H_2O\) vapor molecules on the frozen aerosols as NAT (Type Ia) and ice (Type II) at temperatures suggested by the equilibrium phase diagram of nitric acid solution and water.

Although conceptually plausible, this simple model fails to provide satisfactory explanations for several recent field observations. First of all, balloon-borne measurements of the abundance of nitric acid in the lower Arctic stratosphere revealed that
substantial supersaturation with respect to NAT ($S_{NAT} \geq 10$) is required for the first observation of cloud particles (presumably Type Ia PSCs) [17, 18, 19, 20, 21, 22]. This is consistent with the conclusion of Marti and Mauersberger [113] that there exists a large nucleation barrier to the formation of NAT. Marti and Mauersberger further suggested the possibility of a compositional change of the water-poor hydrates (e.g. NAD and NAM, supposed to form before NAT) toward the more stable trihydrate form. This picture is similar to a model suggested earlier by Worsnop et al. [105]. More recently, Fox et al. [114] reported the finding of a new metastable ternary hydrate, $H_2SO_4 \cdot HNO_3 \cdot 5H_2O$, in coexistence with binary $H_2SO_4 \cdot kH_2O$ hydrates ($k = 2, 3$ and $4$). They also argued with the help of Ostwald’s rule [75] that NAD and the new metastable ternary hydrate were probably more important than NAT at the initial stage of PSC formation.

The DSC results obtained in this experiment have demonstrated the following interesting properties of the ternary acid system. As a general observation, it seems that it is much more easier to supercool a $H_2SO_4$-rich ternary solution than a $HNO_3$-rich solution probably due to the much steeper increase in viscosity with decreasing temperature of the $H_2SO_4$ component. This is also true for the binary acid systems. For instance, $3 \text{ ml}$ samples of $H_2SO_4/H_2O$ solutions with acid concentrations ranging from 50 to 70 wt% were observed to remain in the supercooled liquid state down to temperature as low as 185 K [50] while nitric acid solutions with similar acid concentration would often freeze spontaneously during the cooling process.

The frozen products of the ternary acid systems could be a mixture of ice, acid hydrates (SAT or NAT) and supercooled acid solution. Depending on the thermal history, ternary acid solutions with a substantial amount of $H_2SO_4$ can be easily supercooled all the way down to the ice frost point. On the other hand, it has also been observed that NAT can freeze out from rather concentrated ternary $H_2SO_4/HNO_3/H_2O$ acid solutions even though the lowest temperature is kept above the ice frost point (refer to Figures 4-28 and 4-29). This obviously implies that formation of NAT crystals from ternary acid solutions is also a thermodynamically feasible process in the

$^6$The ice crystals so formed are usually doped with a small amount of acid impurities.
stratosphere.

The interpretation of this observation, however, requires some caution as the exact formation mechanism of NAT cannot be inferred from this particular experiment. One cannot simply rule out the possibility that microscopic ice germs nucleated in the acid solutions also induce the crystallization of NAT, as suggested by Koop et al. [25] In fact, as will be demonstrated in the next section, the liquid-solid transformation of emulsified acid droplets can only be satisfactorily explained with the help of such hypothesis. Finally, the possibility of the coexistence of any metastable ternary $H_2SO_4 - HNO_3$ hydrates with SAT and NAT is also not excluded since there are still several endothermic transition peaks near the ternary eutectic point remain unexplained. One of those peaks may correspond to the formation or melting of the new ternary hydrate suggested by Fox et al. [114].

4.5.2 Crystallization of Emulsified Acid Systems

One of the main advantages of studying phase transition using the acid/oil emulsion system is that all the aqueous droplets are essentially isolated by the oil phase and hence there should be no or only minimum molecular exchange between the droplets during the cooling and warming processes. Furthermore, the results obtained can have a statistical meaning due to the fact that a large number of aqueous droplets ($\sim 10^9$ droplets/cm$^3$) are generally used for each measurement. Assuming the aqueous droplets are uniformly distributed in the halocarbon oil, one can estimate the average distance ($\bar{d}$) between the centers of the droplets using the approximation [115]

$$\bar{d} \approx n_o^{-1/3}$$

(4.41)

where $n_o$ is the number density of the aqueous droplets.

By adopting the value of the average radius $r_{av}$ calculated using Eq. (4.47) on page 138, the number density is found to be $\sim 2 \times 10^{-3}$ droplets/µm$^3$ and hence $\bar{d}$ is approximately 8 µm. However, one has to be very careful about interpreting the meaning of $\bar{d}$ so calculated because of the large polydispersity of the droplets. It
had been reported in the literatures [116] that monodispersity of droplets could be achieved only by the use of high speed rotor mixer (25000 rpm) or ultrasonicator.

The morphology of the emulsified aqueous droplets has been studied using a transmission optical microscope equipped with a cooling stage. Shown in Figure 4-30 and 4-31 are four micrographs taken for a water-in-oil (W/O) emulsion sample (10 wt% deionized water) at various temperatures. Figure 4-30(a) shows the typical size and shape of the aqueous droplets in the emulsion. The dimension of the rectangular box in the figure is approximately 30.4 x 40.9 μm. Although most of the droplets appear to be roughly spherical, some of them (especially the smaller ones) are unmistakably irregular in shape. The reason for this is not clear. It may be due to the relatively high concentration of lanolin in the oil phase.

Shown in Figures 4-30(b), 4-31(a) and 4-31(b) are a sequence of pictures captured during a warming event of the same water-in-oil emulsion sample. The emulsion sample had been cooled down previously to -60 °C just to make sure all the droplets were frozen before the heating scan. The corresponding temperatures for the pictures are -5.2, 0.3 and 5.1 °C, respectively. A tiny drop of the emulsion (≤ 1 μl) placed in an air-tight glass container was used in this experiment. Owing to the poor contrast, it was almost impossible to visually distinguish between the liquid and the frozen droplets. Even the shapes of the droplets remained unchanged. The only observable change during the transition was the proceeding of the melting front, as indicated in Figure 4-31(a) by an arrow.

As a stochastic process, the freezing of the liquid droplets is much more difficult to detect comparing with the melting of the frozen droplets which always happens within a narrow temperature range. Nevertheless, the freezing processes for emulsified acid systems can still be occasionally observed because of the relatively long span of crystal growth time. As already illustrated in Figure 4-4, the whole crystallization process can last as long as 6 - 7 min with a moderate cooling rate of -1 °C/min.

Seven micrographs similar to the one shown in Figure 4-30(a) were analyzed for the droplet size distribution. In order to avoid underestimating the average droplet size, the largest dimension of an irregular droplet was always chosen as the diameter. The
Figure 4-30: Micrographs of the water-in-oil (W/O) emulsion taken at different temperatures during a cooling-heating cycle. (a) $T = 22 \, ^\circ C$ (before the cycle); (b) $T = -5.2 \, ^\circ C$ (during heating).
Figure 4-31: Micrographs of the water-in-oil (W/O) emulsion taken at different temperatures during a cooling-heating cycle. (a) $T = 0.3 ^\circ C$ (during heating); (b) $T = 5.1 ^\circ C$ (during heating).
Figure 4-32: Droplet size spectrum of the water-in-oil (W/O) emulsion. Weight fraction of water is \( \sim 0.1 \). Total particle count and micrograph area are 510 and 76020 \( \mu m^2 \) respectively.

resulting droplet spectrum and the accumulative frequency are shown in Figures 4-32 and 4-33 respectively. The size spectrum of the droplets as seen from the microscope is found to be best represented by the empirical expression [117]

\[
g(r) = ar^2 \exp(-br^2)
\]

(4.42)

where \( g(r) \) is number of droplets with radius \( r \) per \( \mu m^2 \). The constant \( b \) is related to
Figure 4-33: Accumulative frequency of the same water-in-oil (W/O) emulsion as in Figure 4-32.
the average droplet size $r_{av}$ as follows

$$r_{av} = \frac{1}{N} \int_{0}^{\infty} rg(r)dr \quad (4.43)$$

$$= \frac{a}{2Nb^2} \quad (4.44)$$

where $N$, the total number of droplets per $\mu m^2$, is simply

$$N = \int_{0}^{\infty} g(r)dr \quad (4.45)$$

$$= \frac{a\sqrt{\pi}}{4b^{3/2}} \quad (4.46)$$

Substituting Eq. (4.46) into Eq. (4.44) then gives

$$r_{av} = \frac{2}{\sqrt{b\pi}}. \quad (4.47)$$

To estimate the values of the constants $a$ and $b$, one can simply plot $[\ln g(r) - 2\ln r]$ against $r^2$ and fit the points with a straight line as implied in Eq. (4.42) and shown in Figure 4-34. It is found in this way that $r_{av}$ and $a$ are 2.28 $\mu m$ and $8.23 \times 10^{-4}$ $\mu m^{-4}$ respectively.

Before discussing the DSC results, it is important to make sure that there is no appreciable reaction between the acid phase and the emulsifier (i.e. lanolin). Control experiments done without the emulsifier have already demonstrated the inertness of the halocarbon oil for the entire range of acid concentration. Lanolin is a natural compound extracted from sheep wool composed mostly of not well-defined esters and hence the stability of it in concentrated acids is quite uncertain. It is, however, interesting to point out that inorganic esters such as nitroglycerine and dimethyl sulfate are usually prepared by the reaction of alcohols with mineral acids (such as $HNO_3$ and $H_2SO_4$) as described in any organic chemistry textbooks [118]. The possibility of the presence of a tiny amount of alcohol in the aqueous droplets is therefore not excluded.

Shown in Figure 4-35 are the DSC cooling thermograms for two 52.8 wt% nitric
Figure 4-34: Variation of $\ln(g(r)) - 2\ln(r)$ with $r^2$ for the water-in-oil (W/O) emulsion. Also shown is a linear fit of the data.
acid bulk solution samples, one with lanolin immersed in the solution for approximately an hour and one without. Although lanolin did not appear to be soluble in the nitric acid solution, tiny pieces of dust-like particles of lanolin were found floating inside the acid solution after rigorous agitation. No color change was observed during the preparation. It seems that the presence of foreign objects in the acid solution was simply to induce heterogeneous nucleation of NAT (i.e. raising the transition temperature) as illustrated in Figure 4-35 by the arrows. The identity of the frozen mixture at \( \sim -73 \, ^\circ C \) is unclear at this point. Since the cooling thermogram for the acid sample with lanolin also exhibits an exothermic peak, albeit small, at approximately the same temperature, one can tentatively assign the peak at the lower temperature as the eutectic transition of ice and NAT. With this presumption, it would appear that the formation of ice in the sample without lanolin at the eutectic point actually triggers the complete crystallization of the remained acid solution into NAT.

The heating thermograms for the two nitric acid samples are essentially identical and hence only the thermogram for the sample with lanolin is reproduced in Figure 4-36. Also shown are two other heating thermograms of the same sample taken two days and one month after the sample preparation. It is obvious that all three samples have a similar thermogram pattern, viz. a eutectic transition of ice and NAT at approximately \(-42 \, ^\circ C\) and a melting peak of NAT at \(-19 \, ^\circ C\). By comparing the thermograms of the one-hour sample with the two-days sample, one can assume that
the composition of the nitric acid solution had not been changed by the presence of lanolin even two days after the sample preparation. Not only the transition temperatures are the same for both thermograms, the area ratio of the eutectic peak to the melting peak remains the same as well. The same acid solution was also tested one month after the preparation. This time the melting peak shifts slightly to the left while the eutectic temperature remains the same implying that either reactions between the acid and the lanolin or the evaporation of water may have slightly changed the composition of the nitric acid solution. Also the area under the eutectic peak has become comparable to that of the melting peak. To this end, all the DSC experiments employing emulsified acid samples were performed within four hours after the preparation of the samples.

The same method was used to test the stability of lanolin in sulfuric acid solutions. The DSC thermograms for the 5 and 10 wt% sulfuric acid solutions with an excess amount of lanolin are reproduced in Figure 4-37 to 4-40, together with thermograms of acid samples without lanolin as control. All the DSC measurements were performed six days after the preparation of the samples. The color of the acid solutions (with lanolin) remained clear even two weeks after the measurement. As clearly shown in the figures, there is essentially no difference between the transition peaks for the samples with and without lanolin. It also appears that the lanolin in the solution did
Figure 4-37: DSC cooling thermograms of 5 wt% sulfuric acid solution with lanolin taken 6 days after preparation.

Figure 4-38: DSC heating thermograms of 5 wt% sulfuric acid solution with lanolin taken 6 days after preparation.

Figure 4-39: DSC cooling thermograms of 10 wt% sulfuric acid solution with lanolin taken 6 days after preparation.
Figure 4-40: DSC heating thermograms of 10 wt% sulfuric acid solution with lanolin taken 6 days after preparation.

not induce any nucleation of acid hydrates such as SAT, as it did in the case of nitric acid. Also observed in the heating thermograms are the melting peaks at $T > 0 ^\circ C$ due to the acid condensation on the inner side wall of the sample pan, as described previously in Section 4.4.1 (Page 113). The exothermic peak at approximately $-85 ^\circ C$ has also been observed by Ji et al. [119] using a similar technique. They assigned that particular transition to the binary eutectic of ice and SAT, and then concluded that SAT can nucleate in bulk solutions of water-rich sulfuric acid under winter polar stratospheric conditions. The results shown here basically agree with their conclusion.

The glass transition temperature ($T_g$) of the halocarbon oil is around $-150 ^\circ C$ ($123.15 K$) as determined by the DSC while the $T_g$ for the acids is generally in the range of $-120$ to $-135 ^\circ C$. The color of the $HNO_3$ binary acid emulsions appears to be milky yellow. Generally speaking, the higher the concentration of nitric acid, the deeper the yellow color. For cases of extremely concentrated acid (e.g. 77 - 83 wt% $H_2SO_4$ binary acid), the emulsion developed into dark brown color almost instantaneously. The sudden change in color can probably be attributed to the dehydration of lanolin.

Other emulsion systems using fluorosurfactants (Zonyl FSN-100 and FSO-100, Du Pont) instead of lanolin had been tested before the adoption of the above described system. It was initially believed that the excellent chemical inertness of fluorosurfactants would be ideal for our purpose. Unfortunately, it was soon found
out that the solubility of this kind of surfactants in aqueous systems is relatively high ($\geq 0.1 \text{ gSolid/100 gSolution}$) and hence quaternary in stead of ternary systems were obtained. The DSC thermograms shown in Figure 4-41 indicate that the freezing temperature depends strongly upon the amount of fluorosurfactant in the emulsion system. Moreover, the equilibrium melting point of this system shifts slightly to the lower temperature side indicating an enhanced solute effect of the fluorosurfactants.

Shown in Figure 4-42 to 4-59 are the cooling and heating thermograms of the emulsified binary $HNO_3/H_2O$ solutions. A moderate temperature scan rate of $1 ^\circ C/min$ was used for both the cooling and heating processes. This scan rate was chosen with the consideration of two particular requirements in mind. On the one hand, a slower scan rate should be used so as to better simulate the real equilibrium condition. On the other hand, a faster scan rate is required to maintain a certain signal-to-noise ratio. The eutectic and melting temperatures of the emulsion samples are practically the same as those obtained using bulk nitric acid solutions. During cooling, freezing was observed for the composition range $0 - 32.5 \text{ wt}\% HNO_3$ with the absence of glass transition. For the $35 \text{ wt}\%$ emulsion sample, glass transition and freezing were only seen during the warming process. With particular interest is the $40.3 \text{ wt}\%$ case where freezing was observed only in some samples (see Figure 4-51 and 4-52).

Beyond $40.3 \text{ wt}\%$ glass transition was observed during warming through the typical jump in heat capacity associated with the release of $HNO_3$ and $H_2O$ from the glass structure. As can be seen in the kinetic phase diagram of the binary $HNO_3/H_2O$
emulsion system (Figure 4-60), $T_g$ increases linearly with the weight percentage of nitric acid. By extrapolating the freezing temperature $T_f$ down to $\sim -140 \, ^\circ C$, one can define a composition $x^*$ where $T_f = T_g$ such that the emulsified nitric acid solution can only freeze when $x < x^*$ ($\sim 39 \, \text{wt\%}$). Note that $x^*$ is slightly higher than the eutectic composition (33.5 \, \text{wt\%}) of ice/NAT.
Figure 4-42: DSC thermograms of deionized water emulsion system.

Figure 4-43: DSC thermograms of 5 wt% $HNO_3$ binary emulsion system.

Figure 4-44: DSC thermograms of 10 wt% $HNO_3$ binary emulsion system.
Figure 4-45: DSC thermograms of 15 wt% $HNO_3$ binary emulsion system.

Figure 4-46: DSC thermograms of 20 wt% $HNO_3$ binary emulsion system.

Figure 4-47: DSC thermograms of 25 wt% $HNO_3$ binary emulsion system.
Figure 4-48: DSC thermograms of 30 wt% \( HNO_3 \) binary emulsion system.

Figure 4-49: DSC thermograms of 32.5 wt% \( HNO_3 \) binary emulsion system.

Figure 4-50: DSC thermograms of 35 wt% \( HNO_3 \) binary emulsion system.
Figure 4-51: DSC thermograms of 40.3 wt% $HNO_3$ binary emulsion system.

Figure 4-52: DSC thermograms of 40.3 wt% $HNO_3$ binary emulsion system.

Figure 4-53: DSC thermograms of 45 wt% $HNO_3$ binary emulsion system.
Figure 4-54: DSC thermograms of 50 wt% $HNO_3$ binary emulsion system.

Figure 4-55: DSC thermograms of 53.8 wt% $HNO_3$ binary emulsion system.

Figure 4-56: DSC thermograms of 55 wt% $HNO_3$ binary emulsion system.
Figure 4-57: DSC thermograms of 60 wt% $HNO_3$ binary emulsion system.

Figure 4-58: DSC thermograms of 63.6 wt% $HNO_3$ binary emulsion system.

Figure 4-59: DSC thermograms of 65 wt% $HNO_3$ binary emulsion system.
The enthalpy of crystallization \( (E_z) \) for the emulsified nitric acid solutions with concentration ranging from 0 to 32.5 \( \text{wt}\% \) is plotted in Figure 4-61 as a function of the \( HNO_3 \) \( \text{wt}\% \). As illustrated in the figure, \( E_z \) decreases with increasing \( HNO_3 \) \( \text{wt}\% \) in a nonlinear fashion with a minimum close to the eutectic composition of ice and NAT. A simple quadratic equation can be used to describe the data points. This is slightly different from the Tammann diagram of bulk nitric acid solutions [102] where the enthalpy of fusion is plotted instead. Nevertheless, the unmistakable decreasing trend of \( E_z \) still suggests ice as the main product formed during the cooling process.

Figure 4-62 shows the degree of supercooling \( \Delta T \) as a function of the melting \( (T_m) \) and freezing \( (T_f) \) temperatures for the binary \( HNO_3/H_2O \) emulsion system. Both sets of data are approximated by a linear relationship, with \( \Delta T \) changing more rapidly with \( T_m \) than \( T_f \). This is in contradiction to the surmise of Hallett and Lewis [120] who suggested that the maximum supercooling for ice-forming solutions in general would be the same as the maximum supercooling of pure water (\( \sim 40 \, ^\circ \text{C} \)), i.e.

\[
T_f = T_m - 40 \tag{4.48}
\]

As can be seen in Figure 4-63, Eq. (4.48) does not apply to the case of binary nitric acid emulsion with acid concentration ranging from 0 to 35 \( \text{wt}\% \). Instead, the equation

\[
T_f = 1.7979T_m - 250.97 \tag{4.49}
\]

is found to be more appropriate. Both \( T_f \) and \( T_m \) are in Kelvin. The homogeneous nucleation temperature \( T^* \) for a wide variety of glass forming materials have been measured and the results indicate that \( T^* \) for nearly all materials studied lies between 0.75\( T_m \) and 0.85\( T_m \). These two limits are also shown in Figure 4-63 as references. It is quite obvious from the plot that the binary nitric acid emulsion system studied here does not comply with the above limitations if the assumption \( T^* \approx T_f \) can be made.

Sulfuric acid has been known to have a higher tendency to supercool than nitric acid. If the same linear form of Eq. (4.49) can be applied to the case of sulfuric
Figure 4-60: Kinetic phase diagram of binary $HNO_3/H_2O$ emulsion system.
Figure 4-61: Variation of the enthalpy of crystallization with wt\% of HNO$_3$. (Cooling rate = -1 °C/min)
acid, one should expect a slope much greater than 1.7979. Jensen et al. [76] have calculated the theoretical ice freezing temperatures of sulfuric acid using the classical homogeneous nucleation theory. Their predicted freezing temperatures are generally higher than those calculated using Eq. (4.48) and hence may not be applied to the freezing of binary sulfuric acid aerosols. The results obtained in this experiment clearly suggest that the homogeneous freezing temperature for sulfuric acid aerosols (0 - 35 wt%) should always be less than the ice frost point. For sulfuric acid aerosols with concentration greater than 35 wt%, the freezing probability should be extremely small since even nitric acid aerosols do not freeze in that region. Recent study of Ji et al. [121] using binary sulfuric acid emulsions has confirmed our conjecture.

Knowing the importance of nitric acid on the freezing potential of micron-sized sulfuric acid droplets [23, 40], one should also expect a similar effect of sulfuric acid on the supercooling property of emulsified nitric acid solutions. Interesting results from the freezing experiment of Koop et al. [25] on ternary $H_2SO_4/HNO_3/H_2O$ bulk solutions have shown that even a very small amount of sulfuric acid (e.g. 2.5 wt%) can hinder the nucleation of NAT in the ternary acid system. Unfortunately just like all other freezing studies using bulk samples, their results suffer from the lack of statistical significance. Take their solution sample E (7.5 wt% $H_2SO_4$ and 39.5 wt% $HNO_3$) as an example. Their results show that while one of the solution sample E did not freeze at 190.1 $K$ after 25 $min$, another one with the same composition did at 190.9 $K$ after the same period even though the thermodynamic driving force for crystallization is lower for the latter case. The emulsion samples employed in this study do not have this kind of problem as the results are always reproducible.

Emulsified ternary acid solutions with 1 wt% $H_2SO_4$ and 0 - 35 wt% $HNO_3$ were studied with the DSC as described above. The cooling and heating thermograms for these emulsion samples obtained with a scan rate of 1 $°C/min$ are reproduced in Figure 4-64 to 4-71. With the exception of the 35 wt% $HNO_3$ emulsion, all samples show an exothermic peak during the cooling process. The area under the exothermic peaks decreases as the acid concentration increases implying the formation of ice as the main process during cooling. Only the binary ice/NAT eutectic and the ice
Figure 4-62: Degree of supercooling $\Delta T$ as a function of freezing and melting temperatures for the binary $HNO_3/H_2O$ emulsion system.
Figure 4-63: Variation of freezing temperature $T_f$ with melting temperature $T_m$ for the binary $\text{HNO}_3/\text{H}_2\text{O}$ emulsion system.
melting peaks are observed in the heating thermograms. The ternary eutectic peaks are probably too small to be seen, if they exist at all.

DSC thermograms were also taken for ternary acid emulsion samples with 5 wt% H$_2$SO$_4$ and 0 - 35 wt% HNO$_3$ (see Figure 4-72 to 4-78). Unlike the 1 wt% H$_2$SO$_4$ emulsion samples just described, the ternary eutectic transition peak can be clearly seen for many samples, especially those with a higher concentration of nitric acid. Besides the eutectic and melting peaks, also observed is an exothermic peak near -110 °C. This peak is quite similar to the one found near -73 °C in the heating thermograms of bulk ternary acid solutions discussed on page 122. The fact that the exothermic peak occurs 37 °C lower for the emulsion samples is no surprise since all transformations involving nucleation and growth (in this case, crystallization of SAH or solid-solid transition of sulfuric acid octahydrate into SAH) are susceptible to the effect of supercooling. It seems that this ternary system behaves exactly the way as described in Section 4.3.1, i.e. nucleation sites for SAH were activated during cooling which then grew to full crystals of SAH during the heating scan.

The binary kinetic phase diagram in Figure 4-60 is reproduced in Figure 4-79 with additional data from the ternary emulsion systems. The freezing curves for the 10 and 15 wt% H$_2$SO$_4$ ternary emulsion samples are calculated by linearly extrapolating the existing DSC data. The real freezing curves are expected to be lower than the linear estimation. Also plotted in the phase diagram are deliquescence curves calculated for two extreme stratospheric conditions: (1 ppbv HNO$_3$, 10 ppmv H$_2$O) and (10 ppbv HNO$_3$, 1 ppmv H$_2$O) (represented by legends (P$_{na} = 1$; $P_w = 10$) and (P$_{na} = 10$; $P_w = 1$) in Figure 4-79 respectively) at 100 mbar level. The weight percentage of H$_2$SO$_4$ for several selected points on the curves is also indicated for the sake of clarity. Only the glass transition temperatures for the binary nitric acid system are shown in the figure. As expected, the extrapolated $T_g$ for the ice-forming ternary emulsion solutions (< 39 wt%HNO$_3$) decreases with increasing amount of H$_2$SO$_4$ even though the total acid weight percentage remains rather constant. This is of course due to the higher viscosity of sulfuric acid at low temperatures.

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7Refer to Page 26 for the definition of “deliquescence” in this study
Figure 4-64: DSC thermograms of 0 wt% $\text{HNO}_3$ and 1 wt% $\text{H}_2\text{SO}_4$ ternary emulsion system.

Figure 4-65: DSC thermograms of 5 wt% $\text{HNO}_3$ and 1 wt% $\text{H}_2\text{SO}_4$ ternary emulsion system.

Figure 4-66: DSC thermograms of 10 wt% $\text{HNO}_3$ and 1 wt% $\text{H}_2\text{SO}_4$ ternary emulsion system.
Figure 4-67: DSC thermograms of 15 wt% HNO₃ and 1 wt% H₂SO₄ ternary emulsion system.

Figure 4-68: DSC thermograms of 20 wt% HNO₃ and 1 wt% H₂SO₄ ternary emulsion system.

Figure 4-69: DSC thermograms of 25 wt% HNO₃ and 1 wt% H₂SO₄ ternary emulsion system.
Figure 4-70: DSC thermograms of 30 wt% $HNO_3$ and 1 wt% $H_2SO_4$ ternary emulsion system.

Figure 4-71: DSC thermograms of 35 wt% $HNO_3$ and 1 wt% $H_2SO_4$ ternary emulsion system.
The ternary kinetic phase diagram just described can be used to decide whether ternary acid aerosols with an average radius of $\sim 2.3 \, \mu m$ will have a chance to freeze in the lower winter polar stratosphere. To accomplish this, one has to envisage another axis pointing out from the figure for the weight percent of sulfuric acid. In that manner, the freezing boundary of the emulsified ternary acid solutions will be in the form of a three dimensional surface curving downward as it comes out the paper. The deliquescence curves, on the other hand, are represented by two lines spiraling down the figure as the weight percent of $H_2SO_4$ decreases. A close inspection of this picture reveals that the deliquescence lines do not intersect with the freezing surface all the way down to the nitric acid dew (condensation) point $T_d$. At $T_d$, the aerosols begin to swell with a constant weight percent of nitric acid (i.e. the deliquescence curves are continued by two vertical lines dropping from $T_d$ to the frost point of ice $T_{ice}$) as long as the vapor concentrations of both $HNO_3$ and $H_2O$ remain constant in the lower stratosphere. When denitrification does occur, the two deliquescence lines are continued by bending backward to the freezing envelope of the emulsified binary nitric acid solutions [55]. Figure 4-80 is a schematic illustration of what the three dimensional $T - x - y$ phase diagram should look like. It is important at this point to emphasize once again that the freezing surface of ice in this diagram is only valid for droplets with an average radius of $\sim 2.3 \, \mu m$. As a rough guideline, one can therefore regard the aerosols being frozen (i.e. the formation of Type Ia PSCs) if the deliquescence line intersects the binary freezing curve before the temperature reaches the ice frost point ($T_{ice}$). Another important fact that has to be taken into account is that the average size of the aerosols also increases rapidly after passing the dew point of nitric acid $T_d$. That means the volume effect has to be seriously considered since the probability for a density fluctuation needed for the formation of ice germs scales nonlinearly with the droplet volume [75]. In this case, one should expect the freezing curves to shift upward as the temperature goes from $T_d$ to $T_{ice}$, and hence an increasing probability for the aerosols to freeze before reaching $T_{ice}$, i.e. formation of Type Ia PSCs (NAT). Unfortunately, no systematic study of the aerosol size effect on the freezing temperature of binary $H_2SO_4/H_2O$ and ternary $H_2SO_4/HNO_3/H_2O$.
Figure 4-72: DSC thermograms of 0 wt% $HNO_3$ and 5 wt% $H_2SO_4$ ternary emulsion system.

Figure 4-73: DSC thermograms of 5 wt% $HNO_3$ and 5 wt% $H_2SO_4$ ternary emulsion system.

Figure 4-74: DSC thermograms of 10 wt% $HNO_3$ and 5 wt% $H_2SO_4$ ternary emulsion system.
Figure 4-75: DSC thermograms of 15 wt% \( HNO_3 \) and 5 wt% \( H_2SO_4 \) ternary emulsion system.

Figure 4-76: DSC thermograms of 20 wt% \( HNO_3 \) and 5 wt% \( H_2SO_4 \) ternary emulsion system.

Figure 4-77: DSC thermograms of 25 wt% \( HNO_3 \) and 5 wt% \( H_2SO_4 \) ternary emulsion system.
Figure 4-78: DSC thermograms of 30 wt\% HNO\textsubscript{3} and 5 wt\% H\textsubscript{2}SO\textsubscript{4} ternary emulsion system.

acid aerosols has been performed to date.

In the above description, one has naively assumed a binary HNO\textsubscript{3}/H\textsubscript{2}O aerosol model for temperatures lower than \( T_d \). This, of course, is not the case in the lower polar stratosphere, especially after major volcanic eruptions where the total mass of background sulfuric acid can be 10 to 100 times larger than that in the quiescent period. Using a new thermodynamic model, Tabazadeh et al. [55] have estimated the composition of ternary acid aerosols for a wide range of stratospheric conditions. Their results indicate that the amount of H\textsubscript{2}SO\textsubscript{4} in the ternary aerosols can be as high as 10 wt\% for the following volcanic condition: 10 ppbv HNO\textsubscript{3} and 5 ppmv H\textsubscript{2}O at 100 mbar level, 3.6 \( \mu \text{g/m}^3 \) of air of H\textsubscript{2}SO\textsubscript{4}. According to the phase diagram in Figure 4-80, it is therefore less likely for volcanic aerosols to freeze above the ice frost point in the stratosphere as the deliquescence curve tends to move away from the ice freezing surface, in consistent with recent field observation data [122, 123, 124].

In the winter lower stratosphere, the lapse (cooling) rate can sometimes be very large. Typical example is the uplift of moist air by the mountain lee wave in the Arctic. Since the probability of homogeneous freezing decreases with increasing cooling rate [75], one should expect a downward shift of the freezing curves in Figure 4-79 for large cooling rates, leading to a higher chance for the formation of Type III PSCs (smaller ice particles, particle radius \( \sim 2 \mu \text{m} \)) at or below \( T_{\text{ice}} \). Other factors that may also influence the freezing temperature of the ternary acid aerosols include the
initial amount of sulfuric acid and impurities in the aerosols, weight percent of \( HCl \), the composition distribution [125] and the thermal history of the aerosols.

In order to model the crystallization kinetics, one has to have a sound understanding of what actually happens during the cooling of an acid emulsion sample. This can be done by following the cooling path of the emulsion samples in the kinetic phase diagram (Figure 4-81). Consider the freezing of an emulsified binary nitric acid solution with \( X \) wt\% \( HNO_3 \) (point “a”). Upon cooling, the solution remains in the supercooled state until point “b” is reached. At that point, ice begins to form in the binary solution by nucleation and growth until the remaining acid solution have a composition marked by the point “f”. Since this composition is greater than \( X_e \), the remaining liquid is unable to freeze and eventually will transform into nitric acid glass at \( \sim -125 \, ^\circ C \), viz.

\[
\text{a} \rightarrow \text{b} \rightarrow \text{f} \rightarrow \text{glass (} X_e \text{)}
\]

A similar cooling path can be used to described the freezing of an emulsified ternary acid solution with \( X \) wt\% \( HNO_3 \) and 5 wt\% \( H_2SO_4 \):

\[
\text{a} \rightarrow \text{c} \rightarrow \text{g} \rightarrow \text{glass (} X_d \text{)}
\]

According to the DSC cooling thermograms, the transformations from point “b” to point “f” and point “c” to point “g” are not instantaneous, as delineated in Figure 4-81. It takes about 6 - 8 min for the freezing process to complete. For binary (ternary 5 wt\% \( H_2SO_4 \)) emulsion samples with \( X \) very close to \( X_e \) (\( X_d \)) such that the remaining liquid point is lower than point “h” (point “i”), acid glass will form instantaneously right after or even during the formation of ice.
Figure 4-79: Kinetic phase diagram of ternary $H_2SO_4/HNO_3/H_2O$ emulsion system. Also shown in the diagram are the deliquescence curves for two extreme stratospheric conditions.
The importance of cooling rate on the freezing behavior of acid aerosols has already been emphasized in the above discussion. To study this effect, DSC cooling thermograms of ternary acid emulsions scanned using a wide range of cooling rate (from 0.5 to 100 °C/min) are compared in Figure 4-82 to 4-88. The acid concentrations of the emulsion samples are the same as those used for the construction of the kinetic phase diagram in Figure 4-79. As shown in the thermograms, an increase in the cooling rate from 0.5 to 100 °C/min can suppress the freezing temperature by as much as 10 - 15 °C.

The results of the cooling rate experiment are summarized in Figure 4-89 and 4-90, where the freezing temperature is plotted against the cooling rate and the inverse of the cooling rate respectively. Figure 4-90 is often preferred when the small cooling rate region is of particular interest. The plots show that the freezing temperature for all 1 wt% H₂SO₄ ternary emulsion samples with 0 - 30 wt% HNO₃ have a similar dependence on the cooling rate, in contrary to other model systems where the freezing rate has a more profound effect on concentrated solutions [126, 116]. Figure 4-91 is a plot of the freezing temperature as a function of the weight percent of HNO₃ for ternary emulsion systems with the same range of cooling rate. Considering that the freezing temperature T_f for bulk samples with a similar composition is approximately 20 °C higher, one can regard both size and cooling rate as equally important factors in the winter lower stratosphere. The 5 wt% H₂SO₄ ternary emulsion samples basically show a similar cooling rate dependence and hence will not be repeated here.
Figure 4-81: Interpretations of the kinetic phase diagram of binary $HNO_3/H_2O$ and ternary $H_2SO_4/HNO_3/H_2O$ emulsion systems.
Figure 4-82: DSC cooling thermograms of 0 wt% $HNO_3$ and 1 wt% $H_2SO_4$ ternary emulsion system with different cooling rates (in °C/min).

Figure 4-83: DSC cooling thermograms of 5 wt% $HNO_3$ and 1 wt% $H_2SO_4$ ternary emulsion system with different cooling rates (in °C/min).
The extent of crystallization, as defined on Page 99, for two typical ternary emulsion samples is plotted in Figure 4-92 as a function of temperature using the Borchard assumption (Eqs. (4.39) and (4.40)). An onset temperature $T_i$ is observed above which no freezing events are detected. Owing to the fact that $T_i$ depends on a number of crucial factors such as the cooling rate and detector sensitivity, only arbitrarily chosen values are given here as a reference. All emulsion samples studied here exhibit the typical S-shape crystallization curves depicted in Figure 4-92.

The crystallization curves of the ternary emulsion samples are fitted to the non-isothermal JMA transformation equation (Eq. (4.38)) in Figures 4-93 and 4-94. The temperature and time are interchangeable during the fitting because of the use of a constant cooling rate for all the DSC measurements. The value of the JMA coefficient $n$ used in the fitting ranges from 1 to 4, as suggested in Table 4.1. However, it has been found that not all the crystallization curves can be fitted with the value $n = 4$. This immediately makes interface-controlled growth mechanism a less likely candidate for the ternary acid samples studied here. If three dimensional growth and homogeneous nucleation are assumed, the best fitted value of $n$ would seem to be $5/2$. According
Figure 4-85: DSC cooling thermograms of 15 wt% HNO$_3$ and 1 wt% H$_2$SO$_4$ ternary emulsion system with different cooling rates (in °C/min).

Figure 4-86: DSC cooling thermograms of 20 wt% HNO$_3$ and 1 wt% H$_2$SO$_4$ ternary emulsion system with different cooling rates (in °C/min).
Figure 4-87: DSC cooling thermograms of 25 wt% $HNO_3$ and 1 wt% $H_2SO_4$ ternary emulsion system with different cooling rates (in °C/min).

Figure 4-88: DSC cooling thermograms of 30 wt% $HNO_3$ and 1 wt% $H_2SO_4$ ternary emulsion system with different cooling rates (in °C/min).
Figure 4-89: Freezing temperature as a function of cooling rate for ternary emulsion systems with 1 wt% \( H_2SO_4 \) and 0 - 30 wt% \( HNO_3 \).

Figure 4-90: Freezing temperature as a function of the inverse of cooling rate for ternary emulsion systems with 1 wt% \( H_2SO_4 \) and 0 - 30 wt% \( HNO_3 \).
to Table 4.1, the growth of the crystallites would then be diffusion-controlled, as expected for most glass-forming systems. The fitted values of $\Delta H/k$, $T_0$ and $\ln K_0$ for the binary $HNO_3/H_2O$ and ternary $H_2SO_4/HNO_3/H_2O$ emulsion systems are summarized in Tables 4.3, 4.4 and 4.5.

The kinetic approaches to glass formation focuses mainly on how fast must a given solution be cooled so as to avoid the formation of a detectable amount of crystallites. This is drastically different from the structural and thermodynamic approaches where the fundamental properties of materials are assumed to be responsible for the tendency of glass formation. Generally speaking, the kinetic treatments concentrates on the kinetic processes which determine the overall rate of crystallization, viz. the nucleation rate and the crystal growth rate. The information obtained from the above analysis can be used to predict the long term behavior of isothermal crystallization of the acid emulsion systems provided that the simple non-isothermal crystallization model discussed in Section 4.3.3 is valid.
Figure 4-92: Extent of crystallization ($\xi$) as a function of temperature ($T$) for two typical ternary acid emulsion samples. Cooling Rate = $-1 \, ^\circ C/min$. 
Figure 4-93: Non-isothermal Avrami equation fit (Eq. (4.38)) for the ternary emulsion systems with 1 and 5 wt% $H_2SO_4$. 

Figure 4-94: Non-isothermal Avrami equation fit (Eq. (4.38)) for the ternary emulsion systems with 1 and 5 wt% $H_2SO_4$. (Con't)
Table 4.3: Fitted values of $\Delta H/k$, $T_o$, and $\ln K_o$ for the binary $HNO_3/H_2O$ emulsion solutions using the Non-isothermal JMA Transformation Equation (Eq. (4.38)). n/a: data cannot be fitted with confidence.
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Table 4.4: Fitted values of $\Delta H/k$, $T_o$ and $\ln K_o$ for the 1 wt% $H_2SO_4$ ternary emulsion solutions using the Non-isothermal JMA Transformation Equation (Eq. (4.38)). n/a: data cannot be fitted with confidence.
As a first step, we define $\xi_c = 10^{-3}$ as the critical weight fraction such that when $\xi > \xi_c$, the system will be considered crystalline. Otherwise, it is assumed to be in the glassy state. Eq. (4.38) is then rearranged into the following form with the release of the constraint $T = \dot{T}t$,

$$T = T_o - \frac{\Delta H/k}{\ln \left[ -\ln(1-\xi) \right]/K_o t^n}$$

The above equation describes the dependence of temperature on the time required to reach a crystallized weight fraction of $10^{-3}$. The Time-Temperature-Transformation (TTT) curves for ternary emulsion systems with 1 wt% $H_2SO_4$ and 0 - 30 wt% $HNO_3$ are calculated by substituting the values of $T_o$, $\Delta H/k$ and $K_o$ listed in Table 4.4 into

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Figure 4-95: Time-temperature-transformation (TTT) curves for ternary emulsion systems with 1 wt% $H_2SO_4$ and 0 - 30 wt% $HNO_3$.

Eq. (4.50) and are plotted in Figure 4-95. The Avrami coefficient $n$ assumes a value of 5/2, i.e. homogeneous nucleation and 3-d diffusional growth.

As shown in the figure, the TTT curve shifts to the lower right corner as the concentration of nitric acid in the ternary mixture increases from 0 to 25 wt%. This of course implies that longer time and lower temperature are required for a more concentrated acid solution to freeze. It is estimated that an increase in the concentration of sulfuric acid would have a similar or even stronger effect on the TTT curve. Another interesting observation is the rather sharp cut-off temperature demonstrated by the TTT curves above which the freezing of the ternary acid droplets becomes practically impossible. This cut-off temperature again decreases with increasing acid content in the ternary aqueous droplets. Another example with 5 wt% $H_2SO_4$ and 0 - 25 wt% $HNO_3$ can be found in Figure 4-96.

It is important to understand that the TTT curves shown in Figure 4-95 and 4-96 are incomplete since they are all based on a simplified function of $K$ (see Eq. (4.37)). The actual form of the TTT curve should have an extremum or nose which reflects a competition between the driving force for crystallization and the molecular mobil-
Figure 4-96: Time-temperature-transformation (TTT) curves for ternary emulsion systems with 5 wt% $H_2SO_4$ and 0 - 25 wt% $HNO_3$.

The extremum also represents the least time required to form the critical weight fraction ($10^{-3}$) of crystallites. Illustrated in Figure 4-97 are the typical shapes of TTT curves for both isothermal and constant cooling conditions. The more realistic constant cooling curve can be constructed from the isothermal TTT curve, as demonstrated by Grange and Kiefer [127]. The same approach was later applied to the formation of glasses by Onorato and Uhlmann [128]. As expected, a given degree of crystallinity is observed at lower temperatures and longer times than indicated by the isothermal TTT curve. In principle, the constant cooling curve can also be constructed using the $T_c$ data shown in Figure 4-89. However, the increasing uncertainty in $T_c$ at higher cooling rate near the nose makes this method less attractive for the acid systems studied here.

The simplified function of $K$ used in this analysis includes only the crystallization driving force term. To obtain the lower part of the TTT curve, one has to perform isothermal crystallization experiments for the whole temperature range. Although quite accurate, this method is extremely time consuming. A much simpler way is to first quench the acid solution to a temperature below $T_g$ and then warm it up with a
moderate heating rate, as shown by the temperature path "b" in Figure 4-97. As a comparison, the typical temperature path used in this experiment ("a") is also shown in the figure. Obviously, one has to be very careful when selecting the cooling and heating rate as it is a well-known fact that some concentrated sulfuric acid solutions can remain in their supercooled state after several cooling and heating cycles. In other words, the TTT curves for these solutions should be very far away from the temperature axis and hence a much slower cooling or heating rate is needed. Finally, the factors that may be important in determining the phase state of stratosphere acid aerosols at temperatures above the ice frost point are summarized in Figure 4-98.

More recently, Zhang et al. [129] examined the possible formation of sulfuric acid monohydrates (SAM, \(\sim 84.5 \, wt\%\)) as solid surfaces for heterogeneous reactions under typical stratospheric conditions. Their experimental setup involved the visual monitoring of both the freezing and melting processes of a thin film (\(\sim 0.1 \, mm\) thick) of concentrated sulfuric acid (> 75 \, wt\%) coated on the inside wall of a flow tube. Their results show that sulfuric acid solution freezes readily on the glass wall of the flow tube and the frozen product (SAM) remains thermodynamically stable in the
temperature range of 220 - 240 K. Furthermore, the SAM surface has been found to be rather unreactive for processing reactions such as the hydrolysis of $N_2O_5$.

In order to see if Zhang’s results can be applied to liquid microdroplets, emulsions of binary sulfuric acid (77, 80 and 83 wt%) were prepared in the same way as described before and their thermograms (cooling and heating) were recorded with the DSC. The resulting thermograms show no phase changes except the glass transition of the oil phase at approximately -150 °C. As mentioned previously on page 143, such high concentration of sulfuric acid can dehydrate the lanolin in a matter of seconds and it did in the above cases. Although microdroplets could still be seen with a optical microscope, it was not clear whether the concentration of sulfuric acid inside the droplets remained the same or not. Techniques which do not have this kind of complication such as aerosols in a flow tube and low-temperature microscopy are
therefore required to confirm this result.

One may also wonder if the concentration of the acid droplets will change in time due to processes such as diffusion of $H_2O$ molecules from or to the droplets. To study this kind of mass transfer, multiple emulsion systems (A/O/A)\footnote{A/O/A here stands for acid-in-oil-in-acid.} formed by phase inversion of simple acid-in-oil (A/O) emulsions can be used [130]. Briefly, A/O/A systems consist of both the bulk and droplet acid solution phases (see Figure 4-99) and hence two independent signals are observed each representing one of the phases. The transfer of aqueous solution from the droplets (bulk) phase to the bulk (droplet) phase can then be followed by monitoring the area of the peaks. Preliminary experiments using multiple emulsions have shown that the mass of the droplet phase remains rather constant within the time scale of our experiments. However, it is not sure if the same conclusion can be applied to long term isothermal crystallization experiments with a time scale of days or even weeks.
Chapter 5

Conclusion

The DSC results obtained using ternary $H_2SO_4/HNO_3/H_2O$ and binary $HNO_3/H_2O$ bulk samples have clearly demonstrated that it is thermodynamically feasible to form NAT inside supercooled acid solutions at temperatures above the ice frost point. On the other hand, experiments employing emulsified acid samples have shown that even binary nitric acid droplets (average diameter $\sim 4.6 \, \mu m$) do not freeze when the weight percent of acid is greater than $\sim 39 \%$. Under typical polar stratospheric conditions, the weight percent of nitric acid at the condensation point has been estimated to be around 40% to 58%. This implies that Type Ib PSCs can easily remain in the supercooled state down to the condensation temperature of binary nitric acid $T_d$, in consistent with the results of Koop et al. [25] At temperatures lower than $T_d$ but higher than the frost point of ice $T_{ice}$, Type Ib PSCs can transform into Type Ia PSCs if the acid weight percent of the supercooled droplets reduces tremendously due to denitrification of the lower stratosphere. The actual transition temperature, of course, depends upon several uncontrollable factors such as the cooling rate and ambient water partial pressure of the lower stratosphere (refer to Figure 4-98). Consequently, future work should focus on studying systematically the correlations between liquid-solid transition temperature and experimentally controllable parameters such as droplet size and cooling rate.

In view of the strong supercooling property of $H_2SO_4$, one may also have to consider the effect of other minor components such as $HCl$ and $HBr$ on the ho-
mogeneous freezing temperature of Type Ib PSCs. The composition of quaternary $H_2SO_4/HNO_3/H_2O/HCl$ liquid aerosols was recently calculated by Carslaw et al. [56]. Their calculations show that for 5.5 ppbv $HNO_3$, 2.75 ppmv $H_2O$ and 0.55 ppbv $HCl$ at 100 mbar level, the weight percent of $H_2SO_4$, $HNO_3$ and $HCl$ at temperatures close to $T_d$ are approximately 1 %, 20 % and 1 % respectively. Since there are no freezing data for this kind of quaternary system, the concentration of $HCl$ may be too large to be ignored. Another important factor that also needs to be considered in future study is the possible effect of the thermal history of SSAs on their freezing behavior.

The emulsion technique can also be used to measure the rate of heterogeneous nucleation. This can be done by introducing heterogeneous nuclei directly to the aqueous acid phase before preparing the emulsion. Nevertheless, one has to be very careful when choosing the heterogeneous nuclei as some of them may be hydrophobic and hence more likely to stay in the oil phase. Fortunately, this kind of nuclei is very often inefficient nucleating agent. An obvious disadvantage of the emulsion technique is the requirement of surfactants as a stabilizer. This, of course, means that the measured homogeneous nucleation temperature may be slightly higher than the true homogeneous nucleation temperature due to heterogeneous nucleation at the aqueous/oil interface. Other techniques such as low-temperature microscopy and aerosol flow tube experiment are needed to confirm our conclusion.
Appendix A

Derivation of Equations 2.33 and 2.34

Assuming that both $x$ and $y$ in equations 2.17 and 2.18 are continuous and differentiable with respect to $T$ within the range $180K < T < 220K$, we have, after differentiating the two equations

$$0 = \log e \frac{dx}{dT} + \frac{da_0}{dT} + a_1(-\frac{dx}{dT} - \frac{dy}{dT}) + (1 - x - y)\frac{da_1}{dT} -$$

$$\frac{a_2}{dT} - (\phi - 1)\frac{da_2}{dT}$$

(A.1)

$$0 = -\log e \frac{dx}{dT} - \frac{dy}{dT} + \frac{db_0}{dT} + b_1(\frac{dx}{dT} + \frac{dy}{dT}) + (x + y)\frac{db_1}{dT} +$$

$$2b_2(x + y)(\frac{dx}{dT} + \frac{dy}{dT}) + (x + y)^2\frac{db_2}{dT} - b_3\frac{d\phi}{dT} - (\phi - 1)\frac{db_3}{dT}$$

(A.2)

where

$$\frac{da_i}{dT} (or \frac{db_i}{dT}) = \frac{B_i}{T^2}$$

(A.3)

and

$$\phi = e^{(1-y)^8}$$

(A.4)

The coefficients for $a_i$ and $b_i$ (ie. $A_i$ and $B_i$) can be found in Table 2.4. Note that both $P_{HNO_3}$ and $P_{H_2O}$ are considered as constants here. This, of course, can only be true if there is no dehydration and denitrification in the stratosphere. To further
simplify Eqs. A.1 and A.2, we collect terms for \( \frac{dx}{dT} \) and \( \frac{dy}{dT} \) as follows:

\[
\left( -\frac{\log e}{x} - a_1 \right) \frac{dx}{dT} + [8a_2(1 - y)^7\phi - a_1] \frac{dy}{dT} = \left( \phi - 1 \right) \frac{da_2}{dT} - \frac{da_0}{dT} - (1 - x - y) \frac{da_1}{dT}
\]

(A.5)

\[
U \frac{dx}{dT} + [U + 8b_3(1 - y)^7\phi] \frac{dy}{dT} = \left( \phi - 1 \right) \frac{db_3}{dT} - \frac{db_0}{dT} - (x + y) \frac{db_1}{dT} - (x + y)^2 \frac{db_2}{dT}
\]

(A.6)

where

\[U = b_1 + 2b_2(x + y) - \frac{\log e}{(1 - x - y)}\]

(A.7)

Rearranging the above two equations by factoring out \( \frac{dx}{dT} \) and \( \frac{dy}{dT} \) then gives

\[
\frac{dx}{dT} = \frac{WS - VQ}{RV - SU}
\]

(A.8)

\[
\frac{dy}{dT} = \frac{QU - RW}{RV - SU}
\]

(A.9)

where

\[
R = \frac{\log e}{x} - a_1
\]

\[
S = 8a_2(1 - y)^7\phi - a_1
\]

\[
Q = \frac{da_0}{dT} + (1 - x - y) \frac{da_1}{dT} - (\phi - 1) \frac{da_2}{dT}
\]

\[
V = U + 8b_3(1 - y)^7\phi
\]

\[
W = \frac{db_0}{dT} + (x + y) \frac{db_1}{dT} - (x + y)^2 \frac{db_2}{dT} - (\phi - 1) \frac{db_3}{dT}
\]

Both Eqs. A.8 and A.9 are non-autonomous first-order nonlinear differential equations which can only be solved using numerical methods.
Appendix B

Generalized Kelvin Equation for n-Component System

For a n-component system, the Gibbs free energy of formation of a droplet with radius \( r \) can be expressed as

\[
\Delta G = \sum_{i=1}^{n} n_i (\mu_i^l - \mu_i^g) + 4\pi r^2 \sigma
\]  

(B.1)

where \( n_i \) and \( \mu_i \) are the number of mole and chemical potential of the \( i^{th} \) component in the droplet. The superscripts \( l \) and \( g \) refer to liquid and gas phase respectively. \( \sigma \) is the surface tension of the droplet. Equation B.1 represents also the starting point of classical nucleation theory based on the capillarity approximation. At equilibrium,

\[
\left( \frac{\partial \Delta G}{\partial n_i} \right)_{n_1, n_{i-1}, n_{i+1}, \ldots, n_n} = 0
\]

(B.2)

for \( i = 1, 2, \ldots, n \). Combining equations B.1 and B.2 and making use of both Gibbs-Duhem identity and Gibbs adsorption isotherm, we have

\[
\mu_i^l - \mu_i^g + 8\pi r \sigma \frac{\partial r}{\partial n_i} = 0
\]

(B.3)
for $i = 1, 2, ..., n$. To evaluate $\frac{\partial r}{\partial n_i}$, we partial differentiate the total mass of the droplet

$$M_T = \sum_{i=1}^{n} n_i M_i = \frac{4}{3} \pi r^3 \rho$$

(B.4)

with respect to $n_i$. This gives

$$\frac{\partial r}{\partial n_i} = \left( M_i - \frac{4}{3} \pi r^3 \frac{\partial \rho}{\partial n_i} \right) \frac{1}{4 \pi r^2 \rho}$$

(B.5)

The density, $\rho$, of a $n$-component system is a function of $(n - 1)$ weight fractions since $\sum x_i = 1$, where $x_i$ is the weight fraction of the $i^{th}$ component. The total differential of $\rho$ can be written as

$$d\rho = \sum_{i=1}^{n-1} \frac{\partial \rho}{\partial x_i} dx_i$$

(B.6)

where

$$dx_i = \sum_{j=1}^{n} \frac{\partial x_i}{\partial n_j} dn_j$$

(B.7)

The additional quotation mark next to the summation sign in equation B.6 signifies that the $(n - 1)$ summation terms can be any combination of the $n$ components. Substituting equation B.7 into B.6 gives

$$d\rho = \sum_{j=1}^{n} \sum_{i=1}^{n-1} \frac{\partial \rho}{\partial x_i} \frac{\partial x_i}{\partial n_j} dn_j$$

(B.8)

which, by definition, can also be written as

$$d\rho = \sum_{j=1}^{n} \frac{\partial \rho}{\partial n_j} dn_j$$

(B.9)

Comparison of the above two equations implies

$$\frac{\partial \rho}{\partial n_i} = \sum_{j=1}^{n-1} \frac{\partial \rho}{\partial x_j} \frac{\partial x_j}{\partial n_i}.$$  

(B.10)

Before we can make use of equation B.10, we have to decide the set of $(n - 1)$ weight fractions used in the equation. In other words, the final step involves the evaluation
of the term \( \frac{\partial x_j}{\partial n_i} \). By definition,

\[
x_j = \frac{n_j M_j}{M_T}
\]  

(B.11)

There are two possible cases:

1. \( j = i \)

\[
\frac{\partial x_i}{\partial n_i} = \frac{M_T M_i - n_i M_i^2}{M_T^2} = \frac{M_i(1 - x_i)}{M_T}
\]  

(B.12)

(B.13)

2. \( j \neq i \)

\[
\frac{\partial x_j}{\partial n_i} = -\frac{n_j M_j M_i}{M_T^2} = -\frac{M_i x_j}{M_T}
\]  

(B.14)

(B.15)

By choosing the appropriate set of \( x_j \) such that \( j \neq i \), we have

\[
\frac{\partial \rho}{\partial n_i} = -\frac{M_i}{M_T} \sum_{j=1}^{n} x_j \frac{\partial \rho}{\partial x_j}
\]  

(B.16)

and so,

\[
8\pi r \sigma \frac{\partial r}{\partial n_i} = \frac{2M_i \sigma}{r \rho} \left[ 1 + \sum_{j=1}^{n} \frac{x_j}{\rho} \frac{\partial \rho}{\partial x_j} \right].
\]  

(B.17)

Substituting equation B.17 into equation B.3 and using the thermodynamic relationship

\[
\mu_i^l - \mu_i^q = -RT \ln \frac{P_i^r}{P_i^\infty} = -RT \ln \frac{S_i}{a_i}
\]  

(B.18)

then gives

\[
\ln P_i^r = \frac{2M_i \sigma}{RT r \rho} \left[ 1 + \sum_{j=1}^{n} \frac{x_j}{\rho} \frac{\partial \rho}{\partial x_j} - \frac{3}{2\sigma} \sum_{j=1, j \neq i}^{n} x_j \frac{\partial \sigma}{\partial x_j} \right] + \ln P_i^\infty.
\]  

(B.19)

where \( R \) is the gas constant, \( T \) the absolute temperature, \( P_i^r \) the vapor pressure of component \( i \) over a spherical \( n \)-component droplet with radius \( r \), \( P_i^\infty \) the vapor
pressure of component \(i\) over a flat surface of the same \(n\)-component mixture, \(S_i\) and \(a_i\) are the vapor saturation ratio and activity of component \(i\) respectively. Note that there are only \((n-1)\) summation terms in equation B.19 as the term with \(j = i\) is always excluded in the chosen notation.

In the homogeneous-heteromolecular nucleation theory, it is essential to express the critical radius \(r\) as a function of temperature and vapor saturation ratios, \(S_i = P_i^*/P^*_i\). Summing over \(i\) on both sides of equation B.19 gives

\[
r = \frac{2\sigma}{nRT\rho} \sum_{i=1}^{n} \sum_{j=1, j \neq i}^{n} \Phi_{ij} \tag{B.20}
\]

where

\[
\Phi_{ij} = \frac{M_i}{\ln \frac{a_i}{a_j}} \left[ 1 + \frac{x_j}{\rho} \frac{\partial \rho}{\partial x_j} \right] \tag{B.21}
\]

It is obvious that for a single component system \((n = 1\) and \(a = 1\)), both \(\rho\) and \(\sigma\) assume constant value and hence equation B.21 reduces back to the homogeneous-homomolecular case,

\[
r = \frac{2\sigma M}{RT\rho \ln S} \tag{B.22}
\]

since \(\Phi_{11} = M/\ln S\).\(^1\) Equation B.20 can be further simplified by eliminating the constraint \(j \neq i\) in the \(j\) - summation term. To accomplish this, the double summation is visualized as an \(n \times n\) matrix with zero diagonal terms which satisfies the following identity:

\[
\sum_{i=1}^{n} \sum_{j=1, j \neq i}^{n} \Phi_{ij} \equiv \sum_{i=1}^{n} \sum_{j=1}^{n} \Phi_{ij} - \sum_{i=1}^{n} \Phi_{ii} \tag{B.23}
\]

The final expression for \(r\) then becomes

\[
r = \frac{2\sigma}{nRT\rho} \sum_{i=1}^{n} \left[ \sum_{j=1}^{n} \Phi_{ij} - \Phi_{ii} \right]. \tag{B.24}
\]

\(^1\)The condition that \(\Phi_{ii} = 0\) can be easily eliminated by selecting a new set of \(x_j\) which includes the \(j = i\) term specifically.
Appendix C

Ternary Mixture Density

Estimating the density of ternary system $H_2SO_4/HNO_3/H_2O$ using methods 1 and 2 in Section 3.2.2 is straightforward and so only the relevant equations are given here.

1. Addition of volume of three unary, pure components

$$\rho = \frac{\rho_{sa}\rho_{w}\rho_{na}}{x_{sa}\rho_{w}\rho_{na} + x_{w}\rho_{sa}\rho_{na} + x_{na}\rho_{sa}\rho_{w}}$$  \hspace{1cm} (C.1)

where $\rho_{sa}$, $\rho_{w}$ and $\rho_{na}$ are the densities of pure sulfuric acid, water and nitric acid respectively. The weight fraction $x_{sa}$, $x_{w}$ and $x_{na}$ have already been defined in Chapter 2.

2. Addition of volume of two binary aqueous acid mixtures

There are three possible ways of choosing the two binary mixtures:

(a) $H_2SO_4/H_2O$ and $HNO_3/H_2O$

(b) $H_2SO_4/H_2O$ and $H_2SO_4/HNO_3$

(c) $HNO_3/H_2O$ and $H_2SO_4/HNO_3$
The derivation of the equation for the first combination can be found in Chapter 3 and here only the equations for the second and third combination are listed:

$$\rho = \frac{\rho_{sw}\rho_{nw}}{x_{sa}\rho_{nw} + x_{na}\rho_{sw} + \frac{x_{sw}}{2}(\rho_{nw} + \rho_{sw})}$$  \hspace{1cm} (C.2)

where $\rho_{sw}$ and $\rho_{nw}$ are the densities of the binary systems $H_2SO_4/H_2O$ and $HNO_3/H_2O$ calculated at the equivalent binary weight fraction

$$x^b_w = \frac{\frac{x_{sw}}{2}}{x_{sa} + \frac{x_{sw}}{2}}$$  \hspace{1cm} (C.3)

$$x^b_n = \frac{x_{na}}{x_{na} + \frac{x_{sw}}{2}}$$  \hspace{1cm} (C.4)

respectively.
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