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CHEMICAL KINETICS AND MICROPHYSICS OF ATMOSPHERIC AEROSOLS

a dissertation

by

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# CHEMICAL KINETICS AND MICROPHYSICS OF ATMOSPHERIC AEROSOLS

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ABSTRACT: It is now firmly established that aerosols have important health and climate effects spanning local, regional, and global scales. There are however many important aspects of aerosol kinetics and microphysics that are not well understood. The need for more information required to model and develop protective pollution control strategies has motivated an increasing amount of research in this area. Here we present results of research utilizing a novel aerosol mass spectrometer. Techniques were developed in this work to perform detailed kinetic and microphysical experiments using the device. The work includes instrument calibration and signal processing. Using the apparatus, studies were performed measuring the kinetics of oleic acid with ozone. In addition, a model describing aerosols kinetics over a range of conditions was developed. Several preliminary aerosol microphysics studies were also conducted, including water uptake on oleic acid, sulfuric acid, and sulfuric acid coated soot. Experiments designed to probe coagulation of submicron sulfuric acid aerosols were also performed. In an appendix to the thesis, elements of air pollution economics are discussed and applied. A novel result applicable to pollution permit trading is derived.

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# Chapter 1

## Introduction

### 1.1 Importance of atmospheric aerosol kinetics and microphysics

It is now firmly established that aerosols have important health and climate effects, playing roles on local, regional, and global levels. On the local level, aerosols are central to our understanding of vehicular and industrial emissions leading to urban air pollution. One study estimates that mortality rates increase by 1% for every additional  $10 \mu\text{g m}^{-3}$  of particle loading for aerosol diameters less than  $10 \mu\text{m}^1$ . On a regional level, aerosols are transported from areas of high emissions to otherwise clean remote regions of the country, complicating local efforts at air pollution control. On a global level, the importance of heterogeneous chemistry on aerosol surfaces has been demonstrated in the depletion of the ozone layer<sup>2</sup>. In addition, with the increased acceptance of global warming, the radiative effect (both direct and indirect) of aerosols currently constitutes the most poorly understood factor in efforts to model the earth's climate<sup>3</sup>. Chemical kinetic processes determine the compositional dynamics of aerosol particles as they interact with reactive trace gases, whereas microphysical processes primarily determine aerosol size. An understanding of both size and composition dynamics for aerosol systems is required to model their effect on human health and climate.

Aerosols are defined as any airborne particulate matter, solid or liquid, and include dust, fog, smoke, haze, or smog. Primary aerosols are injected into the atmosphere in condensed phase from sources such as soil erosion, oceans, volcanoes, forest fires and industrial processes. Secondary particles form from condensation of select vapor species, such as terpenes and pinenes in forested areas or anthropogenic  $\text{NH}_3$  with  $\text{NO}_2$  (forming nitrate particles) or  $\text{SO}_2$  (forming sulfates)<sup>1</sup>.

## **1.2 Overview of this work**

The work described in this thesis is divided into five major sections for organizational convenience:

**1. The Aerosol Mass Spectrometer – Flowtube apparatus.** The increasing importance of aerosols to our understanding of air pollution problems and climate change has led to rapid advances in instrumentation in recent years. The AMS was developed in part by our group, for aerosol composition and size measurements in the laboratory and in the field. This section describes the operational principle of the device and presents results of experiments characterizing some of its detection properties. This section also provides an overview of commercial instrumentation used in these studies, including the Atomizer used for aerosol generation, the Differential Mobility Analyzer (DMA) used for aerosol sizing, and the Condensation Particle Counter (CPC) used to measure aerosol number densities.

**2. AMS signal processing.** The AMS signal is formed from the vaporization of single particles at a resistively heated surface near the quadrupole mass filter. In this section we develop a framework for converting this signal into aerosol size distributions, accounting

for instrumental effects such as lens transmission efficiency and single particle and/or chopper broadening. This section is especially important for studies of microphysical aerosol processes where the size distribution is changing, such as: nucleation of vapor to form new particles, condensation and evaporation of gas-phase species interacting with the particle surface, and coagulation (or coalescence) of particles to form larger particles.

### **3. A chemical kinetic model for reactive transformations of aerosol particles.**

Previous models of heterogeneous interactions have focused on reactive trace gas depletion in cloud or aerosol particles and droplets.<sup>4,5,6</sup> However, recent laboratory studies have demonstrated that reactive trace gas uptake can significantly transform the chemical composition of condensed phase species, as is evident from recent work on organic aerosols.<sup>7,8</sup> This model focuses on transformation rates within the particle phase. In limiting cases, the model leads to simple analytical expressions for the condensed phase species depletion as a function of aerosol/gas interaction time. The model takes into account gas phase diffusion, mass accommodation, bulk phase chemical reactions, surface reactions and particle phase reactant diffusion from the aerosol interior toward the surface.

### **4. Kinetics of submicron oleic acid aerosols with ozone.**

Oleic acid is one of a group of organic species proposed as an important tracer species for use in source characterization of ambient aerosols<sup>9</sup>. Ozone is an important oxidant in the troposphere, often in concentrations sufficient to cause adverse effects on human health and vegetation<sup>10</sup>. In the presence of oxidants such as ozone, the relative fraction of organic species may change as the particle ages, and new product species are likely to be introduced. This study focuses on the kinetics of oleic acid ( $C_{18}H_{34}O_2$ ) aerosols with

ozone. In addition to kinetic information, data from these studies were used to determine the aerosol size change due to uptake of ozone, assess reaction stoichiometry, and obtain qualitative information about the volatility of the reaction products.

**5. Preliminary microphysical studies using the AMS.** The role of aerosols in cloud formation and precipitation is increasingly acknowledged<sup>11</sup>. Such indirect climate effects due to aerosols have recently been cited as potentially matching the importance of the effects of greenhouse gases<sup>12</sup>. A critical quantity in this regard is the water uptake by an aerosol of a given composition and size. For simple systems such as oleic acid, we show how to measure Henry's law water solubility within the particle, including a preliminary experimental study of this system. We also consider water uptake on salts (for deliquescence or efflorescence studies) and for soot coated with sulfuric acid. Finally a preliminary study of submicron sulfuric acid microphysics is presented. In this study we demonstrate how to separate nucleation, condensation, and coagulation processes. A method is outlined for measurement of aerosol coagulation rates, and the method is applied to preliminary coagulation data.

### **1.3 Thesis outline**

A description of the instrument is provided in Chapter 2. Calibration procedures are developed in Chapter 3. In Chapter 4, a chemical kinetic model for aerosols is presented. This model is applied to results from the experimental aerosol kinetics study (oleic acid) in Chapter 5. A series of preliminary microphysical experiments is described in Chapter 6. The detailed mathematical formulations for Chapter 6 are covered separately in Chapter 7.

Some basic problem solving tools used in air pollution policy analysis are presented in an appendix to the thesis. This includes a novel application of economic theory to the case of polluting firms operating under emission permit trading constraints.

#### **1.4 List of publications**

1. Kinetics of submicron oleic acid aerosols with ozone: A novel aerosol mass spectrometric technique, J. W. Morris, P. Davidovits, J. T. Jayne, J. L. Jimenez, C. E. Kolb, Q. Shi, D. R. Worsnop, W. S. Barney and G. R. Cass, *Geophysical Research Letters*, May, 2002.
2. A chemical kinetic model for reactive transformations of aerosol particles, D. R. Worsnop, J. W. Morris, P. Davidovits, Q. Shi, and C. E. Kolb, *Geophysical Research Letters*, October, 2002.
3. Numerical characterization of particle beam collimation: part II integrated aerodynamic lens-nozzle system, X. Zhang, K. A. Smith, D. R. Worsnop, J. L. Jimenez, J. T. Jayne, C. E. Kolb, J. W. Morris, and P. Davidovits, submitted to *Aerosol Science and Technology*, 2002.
4. Ambient aerosol sampling using the aerodyne aerosol mass spectrometer, J. L. Jimenez, J. T. Jayne, Q. Shi, C. E. Kolb, D. R. Worsnop, I. Yourshaw, J. H. Seinfeld, R. C. Flagan, X. Zhang, K. Smith, J. W. Morris, and P. Davidovits, *Journal of Geophysical Research*, June 2001.

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- <sup>11</sup> Report of the International Panel on Climate Change, 1995.
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