

Atmospheric Pressure Flow Reactor / Aerosol Mass Spectrometer Studies of  
Tropospheric Aerosol Nucleation and Growth Kinetics

Contract DE-FG02-98ER62555

Final Report, June, 2001

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## INTRODUCTION

The objective of this program was to determine the mechanisms and rates of growth and transformation and growth processes that control secondary aerosol particles in both the clean and polluted troposphere. This laboratory program continued the on-going collaboration of the Aerodyne Research, Inc. (ARI) and the group of Prof. Paul Davidovits in the Department of Chemistry at Boston College (BC). The experimental plan coupled the ARI aerosol mass spectrometer (AMS) with the BC chemical ionization mass spectrometer (CIMS) to provide simultaneous measurement of condensed and particle phases. The first task investigated the kinetics of tropospheric particle growth and transformation by measuring vapor accretion to particles (uptake coefficients, including mass accommodation coefficients and heterogeneous reaction rate coefficients). Other work initiated investigation of aerosol nucleation processes by monitoring the appearance of sub-micron particles with the AMS as a function of precursor gas concentrations.

The aerosol growth experiments were performed by preparing flows of aerosols with known size distributions and compositions and monitoring their growth rates and composition changes with aerosol mass spectrometry as levels and combinations of condensable and reactive gases were manipulated. The experimental apparatuses is schematically shown in Figure 1. By quantitatively mixing aerosols of known size (selected with a differential mobility analyzer, DMA) with gases at known concentration for variable times (varying between a fraction of a second and minutes), aerosol growth and reaction rates can be determined and expressed as uptake coefficients which then can be applied to atmospheric aerosol models.

This experimental approach of this program centered on the AMS particle detection system, which separates particle vaporization and subsequent vapor ionization in a quadrupole mass spectrometer. The particles are flash vaporized in a heated oven (300-1000C), the resulting vapor plume injected into an electron impact ionizer, and the positive ions then analyzed in a quadrupole mass filter. The advantage is that the thermally produced vapors are linearly detected with the quadrupole mass spectrometer. Key to this is the flash vaporization process, which depends critically on oven design, which has continued to evolve during the past year. Understanding and quantifying the vaporization process is essential to absolutely determine the amount of deliquesced water and organic vapor in the sub-micron aerosol particles. This applies both to laboratory and field aerosol measurements and in fact the DOE sponsored laboratory program has taken advantage of parallel development of the AMS for ambient aerosol sampling.

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Three projects were investigated during the program: (1) Ozonolysis of oleic acid aerosols as model of chemical reactivity of secondary organic aerosol; (2) Activation of soot particles by measurement deliquescence in the presence of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and water vapor; (3) Controlled nucleation and growth of  $\text{H}_2\text{SO}_4$  aerosols. The first and last established additional collaborations with the groups of Prof. Glen Cass of Caltech (now at Georgia Tech) and Prof. Greg McRae at MIT, respectively. The Cass group has much experience in the analysis of urban aerosols, particularly using oleic acid as chemical marker. The McRae group has developed a numerical model accounting for nucleation, coagulation and growth of aerosols which we have applied to our experiment.

These projects are continuing. Future work will add uptake of  $\text{NH}_3$  vapor to the  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  aerosol system. Organic experiments will be extended to include combinations of aliphatic, aromatic and oxygenated hydrocarbons and mixtures thereof with inorganics. These AMS experiments have the potential to uniquely resolve the kinetics of aerosol microphysics under controlled laboratory, flow tube conditions. Moreover, in the future, as our AMS is deployed for field measurements we hope to relate the laboratory and field studies, both to better characterize ambient aerosols and to understand transformation processes in the atmosphere.

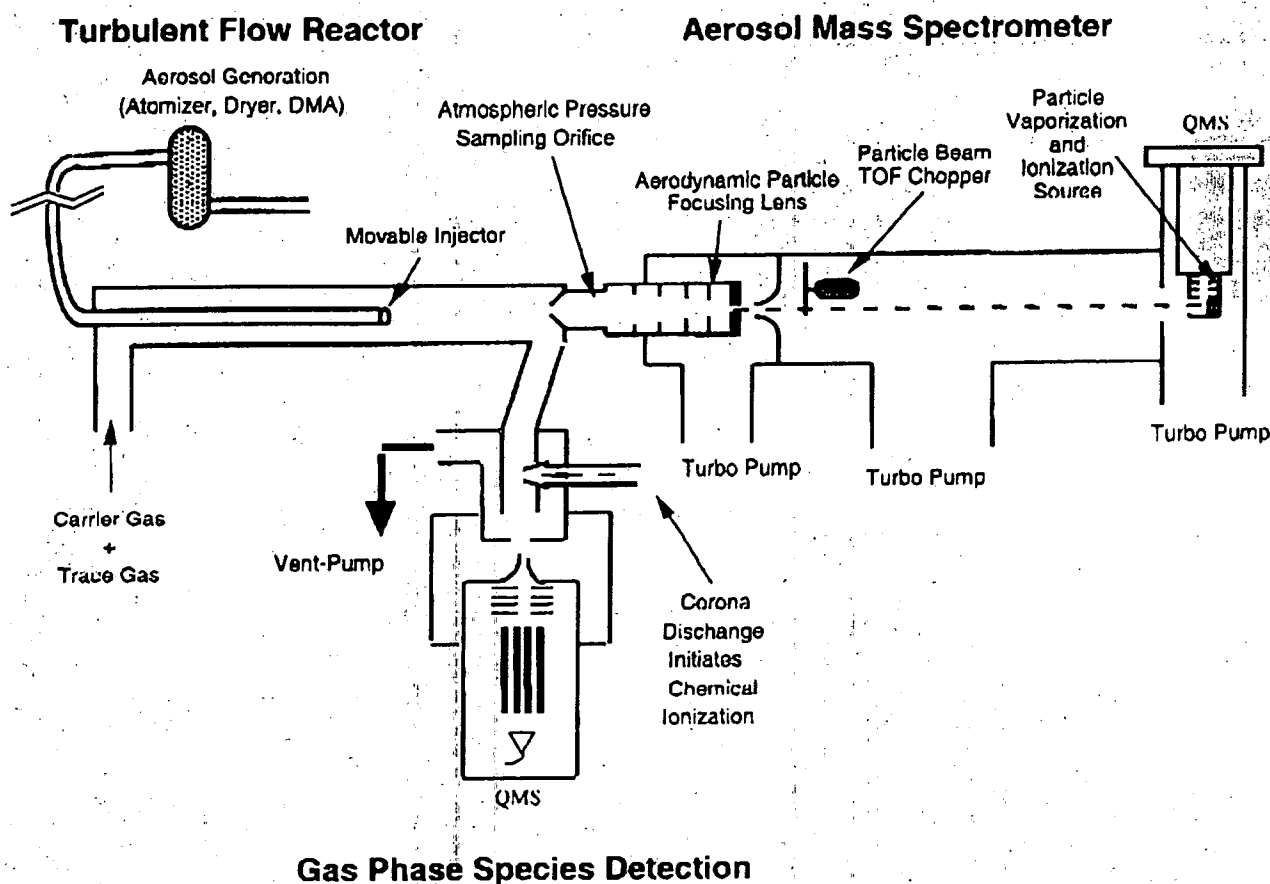


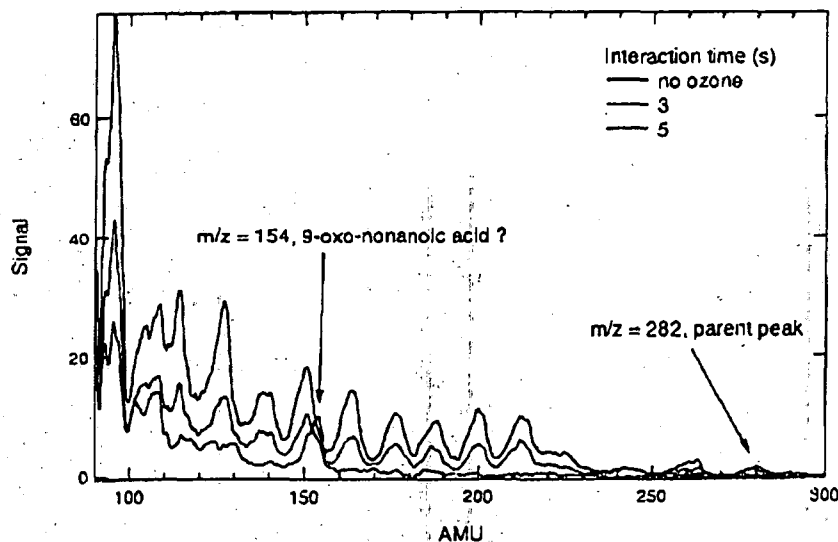
Fig. 1 Schematic of atmospheric aerosol flow reactor coupled to the aerosol mass spectrometer (AMS).

## 1. Ozonolysis of Submicron Oleic Acid Particles

The first detailed experimental study utilizing the aerosol flow reactor (Fig. 1) has been the ozonolysis of oleic acid. Oleic acid has been identified as a chemical marker of meat smoke particles for tracking urban aerosol emissions. However, its utility as a marker depends on its atmospheric lifetime. Oleic acid is a C18 carboxylic acid with an alkene bond at C9 that is susceptible to attack by  $O_3$ . The primary product for such ozonolysis in the condensed phase is expected involve ozone insertion to form an epoxide or ozonide which is then likely to degrade into C9 mixed acids, aldehydes or esters. Indeed we have observed oleic acid reaction and appearance of possible products. We present these preliminary results to illustrate the gas to particle transformation kinetics measurable with the aerosol flow reactor.

Sub micron oleic acid aerosols are generated by atomizing a solution of oleic acid dissolved in methanol. The methanol evaporates as the aerosols are swept through a diffusion dryer, leaving the oleic acid aerosols which are size selected with a DMA. Sized particles then flow into the movable injector. The distance between injector and the AMS sampling inlet (and the carrier gas flow rate) determines the interaction time for the ozone and oleic acid. Low Reynold's numbers ( $\sim 40$ ) provide laminar flow conditions in the reaction zone. The geometry and flow rates within the flowtube have been optimized so that particles which are sampled into the AMS have well defined drift velocities, minimizing particle acceleration near the injector exit and sampling inlet. This in turn allows accurate calculation of the interaction time.

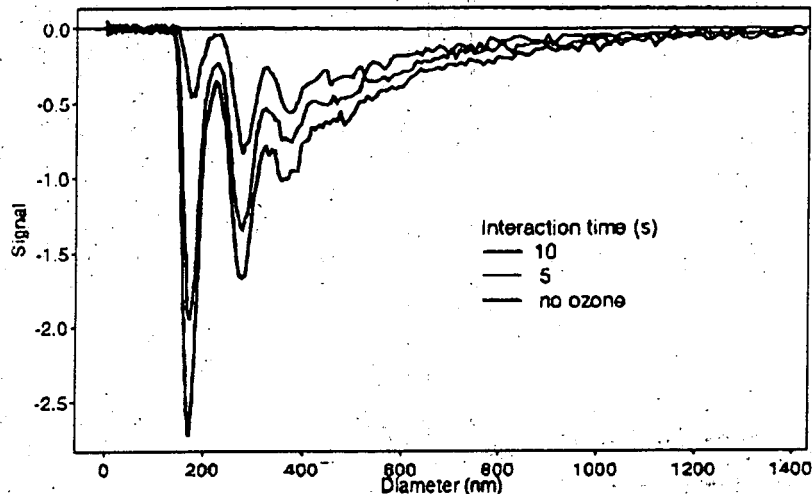
Figure 2 shows scans of the mass spectra up to mass 300 for oleic acid particles after various interaction times with ozone. These spectra were recorded by blocking and unblocking the particle beam and subtracting the "OFF" from the "ON" signals. For the pure oleic acid spectrum (no added ozone) the  $m/z = 282$  is labeled, indicating the parent peak of oleic acid. Upon addition of  $O_3$ , all  $m/z$  peaks above 160 amu are depleted.



masses ( $m/z = 154$  in particular) differs, indicating the presence of reaction products. The observed spectra could be explained by production of C9 products from the C18 oleic acid reactant, though fragmentation in either the particle vaporization or ionization detection processes may preclude definite species identification.

Figure 2 Representative mass spectra of oleic particles after exposure to  $O_3$  gas at  $\sim 10^{15}$  molecule  $cm^{-3}$ .

Figure 3 displays the size dependent data acquisition mode. The mass spectrometer was set to  $m/z=263$  (see fragment in Fig. 9) and particle diameter measured via TOF with the



mechanical chopper in place. The three peaks in the spectrum are due to multiple charging effects in the DMA corresponding to ~180, 300 and 400 nm particles (different size particles with 1, 2 and 3 charges all have the same mobility as selected by the DMA). From this plot it is clear that the oleic acid reaction rate is size dependent with smaller particles reacting faster.

Fig. 3. Size dependent reactive depletion of oleic acid particles (monitored at  $m/z = 263$  amu) exposure to  $O_3$  gas at  $\sim 10^{15}$  mol  $cm^{-3}$ .

Figure 4 plots the fraction of oleic acid remaining as a function of time for the three sizes seen above. (The fraction remaining is simply calculated from the ratio of the  $m/z=263$  signal with and without added ozone for each of the peaks in the size distribution in Fig. 10). The size dependent curves fit to the data are from Case 3a above, fit for product  $H(Dk_2)^{1/2} = 0.04$  M $^{1/2}$  cm s $^{-1}$  atm $^{-1}$ . Calculations with the fit parameters show a 200nm particle composed purely of oleic acid will have a lifetime of about 20 minutes in a polluted atmosphere with 100 ppb ozone.

Such a short lifetime is likely an overestimate of the atmospheric reactivity of aerosol oleic acid, if only because pure oleic acid is not representative of actual particles. In fact, experiments on particles with stearic acid impurity indicate that the observed rate is measurably slower.

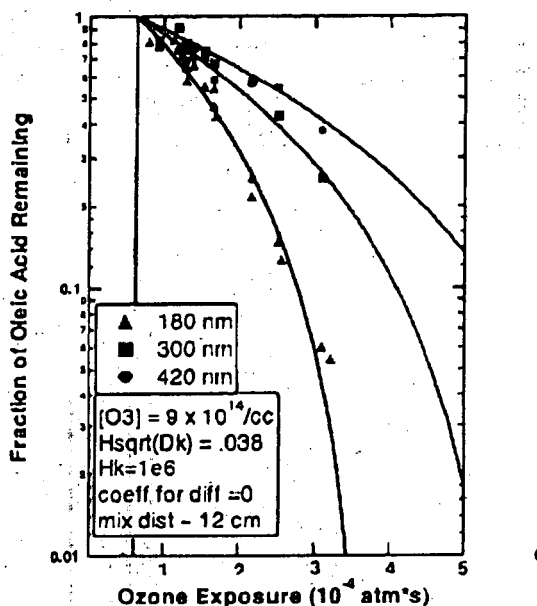


Fig. 4 Oleic acid decays (see Fig. 3)

These results are currently being written in a manuscript that will include detailed kinetic modeling of ozone/oleic acid reactivity. Extensive measurements, over a wide range of particle size and ozone concentration, indicate that ozone reactivity has a complex size dependence; in particular, at large sizes ( $\geq 600$ nm) reaction slows somewhat, due to diffusion limited transport of oleic acid from within the particle. Overall, these results indicate that atmospheric oleic acid lifetimes will depend on gas and condensed phase concentrations and aerosol morphology.

## 2. Acid and Water Condensation on Soot

AMS experiments have measured kinetic parameters relating to soot particle activation by  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$  vapors. This involved the development and characterization of a flame source of fresh soot particles that generate number density distributions that peak in the size range of 50 to 200 nm diameter depending on the fuel/air ratio. The apparatus is schematically shown in Fig. 5. Fresh soot particles generated from a propane flame were injected into an aerosol flow reactor. The particles could be exposed to sulfuric acid vapor and/or water vapor for a controlled interaction time in the flow reactor. The aerosol was then analyzed at the exit of the flow reactor by the AMS to determine the amount of acid and water taken up by the soot. The acid vapor concentration was set by controlling the temperature of a liquid acid reservoir located inside the flow reactor and water vapor was added from a bubbler source. The acid vapor concentration was set by controlling the temperature of a liquid acid reservoir located inside the flow reactor and water vapor was added from a bubbler source.

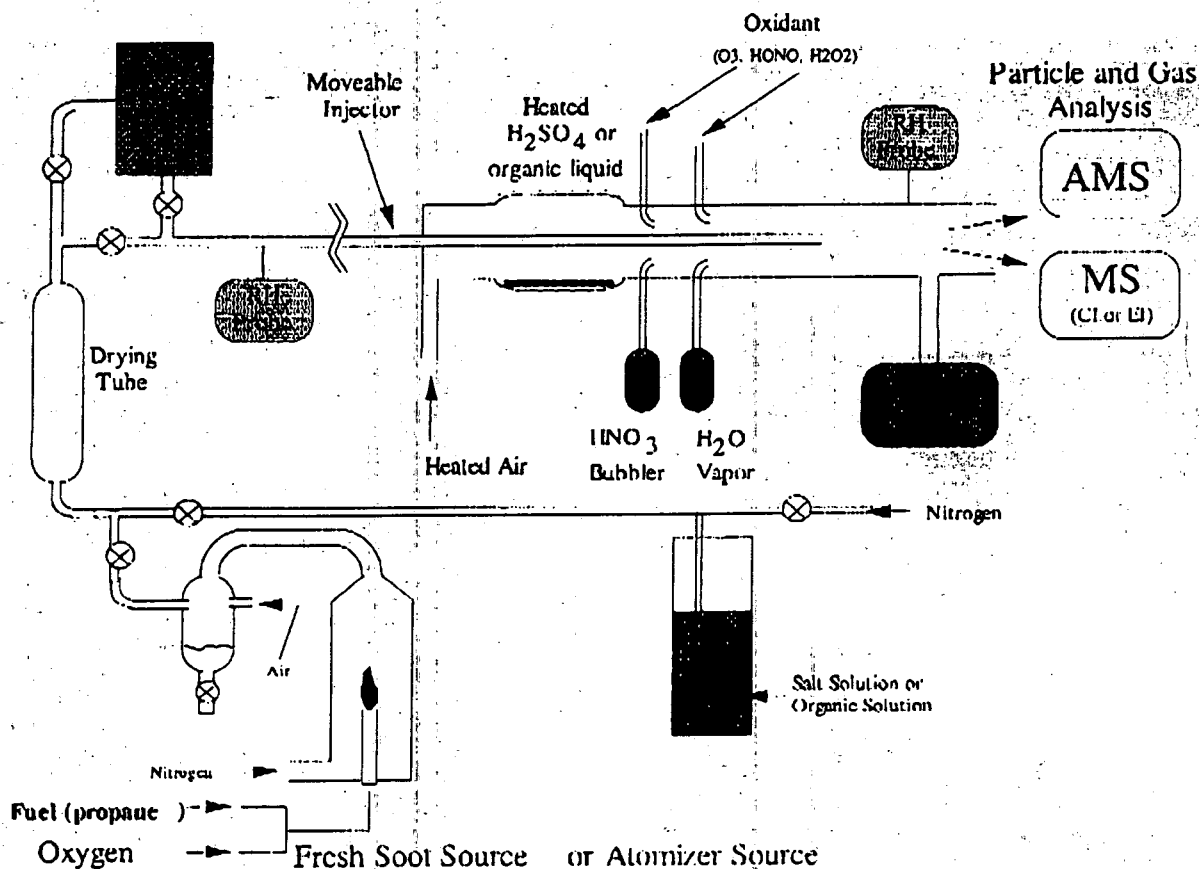


Fig. 5 Schematic of atmospheric aerosol flow reactor coupled to a flame source of soot particles.

In this series of measurements the mass of sulfuric acid and water vapor taken up by the soot particles was determined from the quadrupole mass spectrometer ion signals following particle flash vaporization and electron impact ionization of the vaporized species. Fig. 6 plots the sulfuric acid mass as a function of the acid vapor concentration under conditions where the soot particle loading in the reactor was held constant. As is observed the mass of sulfuric acid vapor taken up by the soot varies linearly with the acid vapor concentration exposed to the soot particles.

Aerosol size is also measured by the AMS via a time-of-flight (TOF) measurement shown in Fig 7. For this case the soot aerosol loading in the flow reactor was again kept constant, the  $\text{H}_2\text{SO}_4$  and  $\text{H}_2\text{O}$  vapor levels were varied and the quadrupole was tuned to  $m/z = 18$  ( $\text{H}_2\text{O}$ ) to monitor changes in particle hydration. At low  $\text{H}_2\text{SO}_4$  vapor no water signal is observed (solid line Fig 7) in the particle TOF spectrum, even when the relative humidity (RH) is increased to 50%. Water in the particle is observed when the acid source temperature is increased to 137 C (dotted line) and increases further as water vapor is added to the flow in addition to the acid vapor (dashed line). These results illustrate that only upon activating the soot with sulfuric acid, is water vapor readily taken up and that fresh untreated soot alone is ineffective in taking up water vapor.

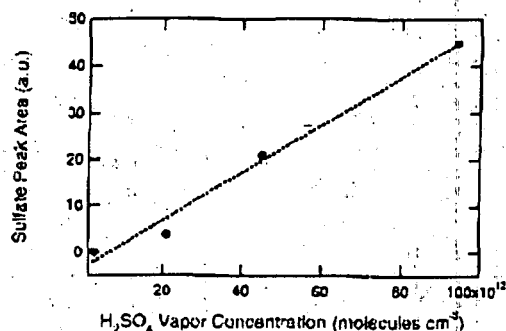


Fig 6. Data illustrating linear uptake of  $\text{H}_2\text{SO}_4$  on soot particles as a function of  $\text{H}_2\text{SO}_4$  vapor concentration in flow reactor.

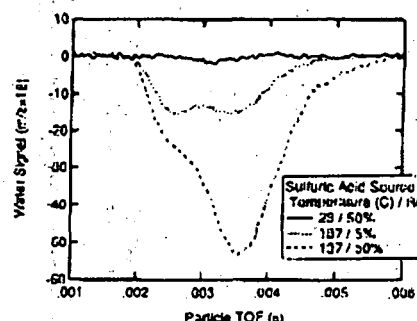


Fig 7. Detection and uptake of water vapor on sulfuric acid coated and uncoated soot aerosol at 5% and 50% relative humidity.

These experiments using propane flame generated soot have measured uptake of gaseous  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  giving uptake coefficients of  $>0.1$  and  $\sim 10^{-4}$ , respectively. Consistent with other studies,  $\text{H}_2\text{SO}_4$  uptake enhances the condensation of water, effectively activating the soot as condensation nuclei, while  $\text{HNO}_3$  uptake does not. Future work will extend the experiments to investigate the heterogeneous chemistry of soot (and other organics) with reactive trace gas species such as  $\text{NO}_x$ ,  $\text{SO}_x$  and  $\text{HO}_x$  and other key atmospheric oxidizing or condensable gases.

### 3. $\text{H}_2\text{SO}_4$ Aerosol Nucleation and Growth

Preliminary experiments have monitored the nucleation and growth of sulfuric acid sub-micron particles. The experiments were performed using the apparatus in Fig. 5 with the soot particle source removed. Dry air was passed over the heated sulfuric acid reservoir. The appearance of aerosol particles was monitored as a function of reservoir temperature. Results are plotted in Fig. 8 for temperature range of 103 to 137C. The mass of observed aerosol clearly increases with increasing temperature. In fact, the integrated mass of the aerosol is approximately proportional to  $\text{H}_2\text{SO}_4$  vapor pressure over the reservoir.

The key question is what processes are controlling the formation of the aerosols in Fig. 8, namely what combination of aerosol nucleation, coagulation and growth can explain the observations. The experimental results have inspired a collaboration with Prof. Greg McRae of the Department of Chemical Engineering at MIT. The MIT group has much experience in numerical modeling of such aerosol microphysical processes. The results of such modeling



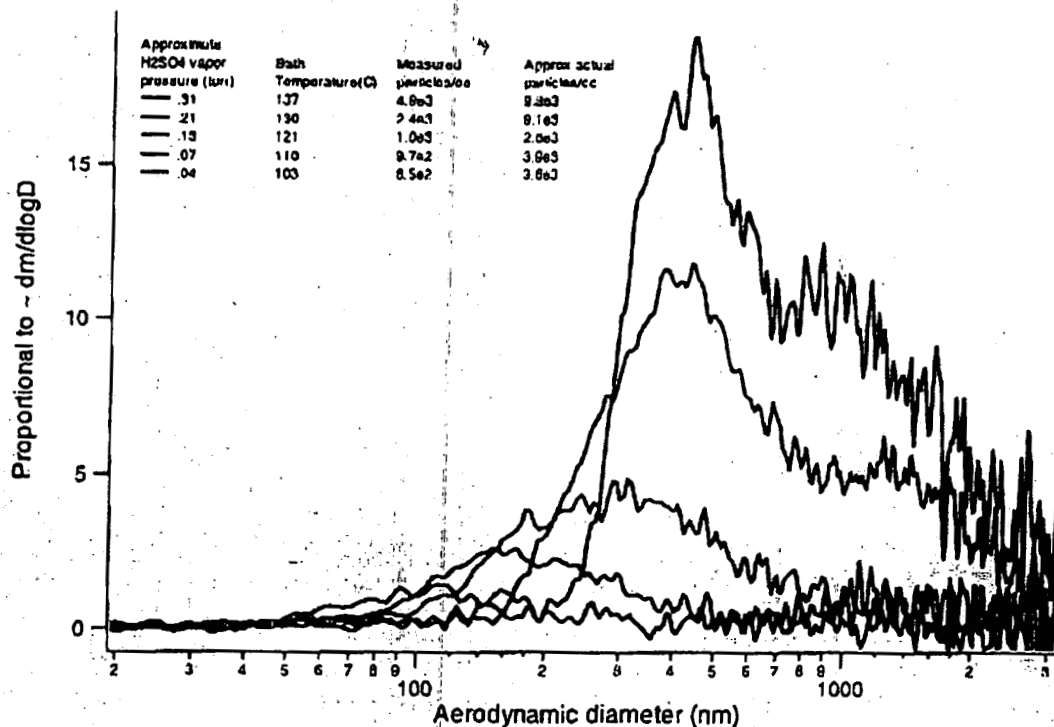


Fig. 8 Nucleation and condensation growth of H<sub>2</sub>SO<sub>4</sub> aerosols

applied to our experimental conditions are plotted in Fig. 9 as aerosol number density distributions. Noting that diameter scales of such number density distributions are effectively multiplied by a factor of two when converting to mass weighted scales such as in Fig. 8, the agreement between the experimental and model distributions is excellent.

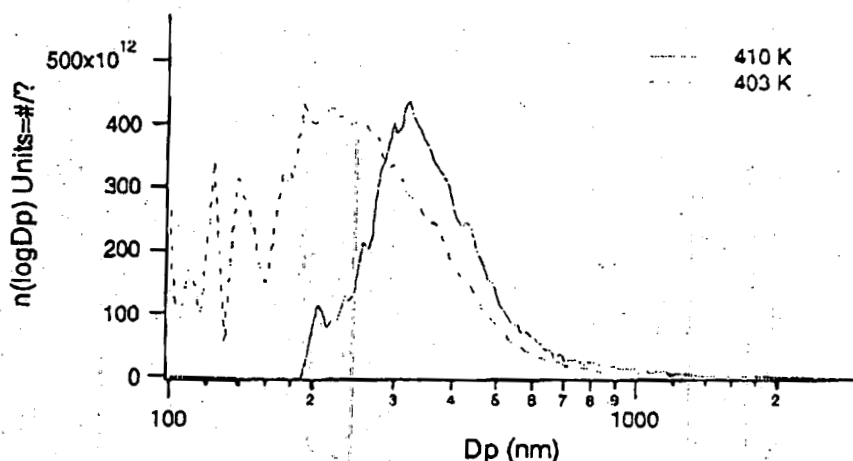


Fig. 9 Model of nucleation and condensation growth of H<sub>2</sub>SO<sub>4</sub> aerosols

The model calculations show that nucleation of new particles followed by growth by vapor condensation control the evolution of the laboratory aerosol system. In particular, the calculations indicate that coagulation is not significant under these conditions. In fact, the calculation indicate that these experiments can provide a useful test of nucleation models. More experiments are planned to better quantify the aerosol mass loading and temperature/flow conditions in the flow reactor.