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The Environmental Control of Individual Aqueous Particles in a Cubic Electrodynamic Levitation System

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ABSTRACT. The experimental investigation of aerosol particles often requires special apparatus to ensure that the walls of the system interfere minimally with the measurements. Electrodynamic levitation offers an attractive approach because the particle, when suitably charged, is held away from the system walls by time-dependent electric fields. A new electrodynamic levitation system has been developed expressly for investigating aqueous particles in controlled gaseous environments. A cubic cell was used in conjunction with the carefully controlled introduction of gas into the cell to form a wall-less flow reactor that is ideal for thermodynamic and kinetic studies involving reactive reagents. Unlike most previous cell configurations, the cubic geometry permits three-axis position control of the particle and an ability to measure the gravitational and drag forces simultaneously and independently when the gas flow is horizontally aligned. Preliminary results at room temperature of the mass gained by salt and sulfuric acid particles exposed to various humidities show the basic characteristics of the cell. New results with sulfuric acid particles exposed simultaneously to the vapors of water and nitric acid show that nonvolatile and volatile solutes cause aqueous particles to behave in qualitatively different ways. Such results confirm that cloud formation in the atmosphere should be enhanced by the presence of soluble trace gases under suitably low-temperature conditions.


INTRODUCTION
The electrodynamic levitation of individual particles has become an attractive means for investigating the properties and behavior of aerosol particles under controlled environmental conditions. In an electrodynamic levitation system (ELS) a particle with suitable charge is trapped in a localized region of space by a time-varying electric field that generates a potential well with restoring forces that act radially inward (March and Hughes, 1989). The particle is thereby kept well away from the walls of the containment cell, allowing it to respond only to the properties of the gaseous medium.

Prior applications of the trapped-particle technique span a wide range of research topics. Because the particles confined in the cell of an ELS necessarily possess excess electric charge, a natural area of inquiry has been the influence of charge and electric fields on the Rayleigh instabilities...
of water drops (Berg et al., 1970; Davis and Bridges, 1994), as has the study of photo-electron emission from various solids (Arnold and Hessel, 1985). The optical properties of various substances have also been conveniently measured (Davis and Periasamy, 1985; Tang and Fung, 1989; Tang and Munkelwitz, 1991a; Essien et al., 1992). Through proper control of the gas surrounding the particle, one can also explore various gas–particle interactions. When near-equilibrium conditions are maintained, water activities and deliquescence points of various salts can be measured readily (Cohen et al., 1987a,b,c; Tang and Munkelwitz, 1978,1984, 1993; Andrews and Larson, 1993). With appropriate precautions, some time-dependent phenomena can also be investigated, such as chemical reactions (Ray et al., 1991; Rassat and Davis, 1992; Foss and Davis, 1994) and droplet growth or evaporation rates (Rubel and Gentry, 1984; Davis and Ray, 1980; Saageev et al., 1986; Fung et al., 1987; Tang and Munkelwitz, 1991b). The diversity of successful studies attests to the strength of the trapped-particle technique.

The system described here is a conceptual descendant of much earlier work in particle confinement. Paul and Raether (1955) were among the first to explore electrodynamic means to localize ions and charged particles in space. Subsequent developments employed the principles of nonuniform and time-varying electric fields to trap particles using a wide variety of electrode configurations, including hyperboloidal endcaps above and below a hyperbolic ring (Wuerker et al., 1959a; Davis and Ray, 1980), spherical end electrodes inside a cylinder (Berg et al., 1970), spherical-void electrodes (Arnold and Folan, 1987), and ring-shaped electrodes in various arrangements (Berg et al., 1970; Weiss-Wrana, 1983; Davis et al., 1990; Ray et al., 1991). Of special interest to the evolution of our system is the cubic design developed initially by Wuerker et al. (1959b) and later by Zaritskii et al. (1971). Separate alternating (AC) voltages from a three-phase power supply were applied to the three pairs of opposing faces of the cell. A constant (DC) voltage was superimposed onto each of the AC voltages, thereby achieving independent three-axis positioning of the particle within the cell volume. Considerable simplification of the cubic design has been achieved by Kendall et al. (1991), who showed that the three-phase AC voltage arrangement could be equivalently replaced by a two-phase drive.

The purpose of this paper is to describe the experimental system, founded on the cubic-electrode principle, that has been developed for investigating the influence of volatile solutes on the chemical equilibria of aqueous particles. The ELS and its supporting subsystems are described in the next section, followed by a presentation of data showing the effect that nitric acid has on the size of sulfuric acid particles. The design should prove valuable for applications in a number of scientific and engineering disciplines.

EXPERIMENTAL SETUP AND METHODS

General Description of Apparatus

The cubic arrangement of electrodes in an ELS offers several advantages for the study of volatile or reactive components, especially when interactions of those compounds with the walls of the system have the potential for unfavorably influencing the outcome of the experiments. As illustrated in Fig. 1, each face of the ELS cell is used for interfacing to the other subsystems that make up the complete experimental system. The top face affords a convenient place for launching the particle, whereas the bottom face is used for illuminating the particle, in our case by the 488-nm line of an argon-ion laser (Spectra Physics 165). Radiation scattered from the particle is gathered through the large, flat “front” and “back” faces in order to view the location of the particle and characterize it via spectroscopic means, respectively. The environmental gas is introduced through the “right-hand” side of the cube, and its properties are determined immediately upon ex-
iting the cell through the "left-hand" face, as viewed in Fig. 1. A computer (286 PC) is used optionally for controlling the levitation electronics and flows when needed, while another (486 PC) serves as the main interface to the spectrometer (Spex 270M).

The levitation cell itself has undergone some development over the course of the investigation. The first version formed a relatively open cube with unsealed edges and electrodes made of conductive glass ("front" and "back") and nickel mesh (other four sides). Some data were taken with this first cell, but a new version was constructed in order to accommodate the introduction of reactive trace gases. The description here focuses on the design and construction features of the second-generation cell.

This cell incorporates several important design features. The body of the cell was constructed of machineable glass (Macor) and joined together with o-ring seals (silicone). Each face of the cubic volume is 2.5 cm across and includes an electrode. Electroformed gold mesh (Buckbee-Mears), 1.5 cm on a side, is used as the electrode material on all but the "right-hand" face, the side used for the introduction of the carrier and reactive trace gases. As shown in Fig. 2, the electrode for this face is a series of vertically aligned tubes that also serve to introduce the reactive gases. The four lateral electrodes, those lying in vertical planes, are supplied with AC voltages between about 300 and 1500 V (peak), depending upon the degree of trapping desired. A phase lag of 60° exists between the AC voltages applied to the front-back and left-right pairs of faces so as to achieve the equivalent of a three-phase drive (Kendall et al., 1991). The frequency can be varied from less than 20 to about 500 Hz. Each pair of opposing electrodes also receives a DC voltage difference between 0 and ±250 V in order to position the charged particle within the cell independently along any of the three Cartesian coordinate axes. Two of the three DC voltages can be controlled by computer (286 PC) in order to maintain the particle precisely in the electrical center of the cell as its mass changes in response to varying environmental conditions. The feedback loop for such applications is an automatic video-image tracking device (Iscan) that monitors the video signal coming from a camera viewing the particle from the side. Additional information about the electronic design and distribution of electric fields in the cell are provided by Allison and Kendall (1996).

As with several other systems (e.g., those of Davis and Periasamy, 1985; Davis et al., 1987; Cohen et al., 1987a; and Andrews and Larson, 1993), we actively introduce a gas into the levitation cell in order to maintain a supply of water vapor or chemical
FIGURE 2. An expanded view of the cubic levitation cell in perspective. The cutaway shows details of the injector grid (dark vertical lines) used to introduce reactive gases into the main flow. The levitated particle (circle) is maintained in the geometrical center of the cell as the environmental gas flows (arrow) through the cell. Electrodes and windows in the cell walls are not shown.

reagents to the particle under investigation. As indicated in Fig. 2, the gas flow in our system is brought in horizontally so that the drag force vector is perpendicular to the gravity vector. Each of these physical forces is counteracted by appropriate adjustment of the relevant DC voltage to force the particle back to the electrical center of the cell, where the net force on the particle approaches zero and the influence of the AC field is minimal.

Under such balanced conditions, the measured DC voltages allow us to calculate both the magnitude of charge on a particle and its mass. If $E_v$ is the magnitude of the vertical electric field (potential gradient) in the center of the cell used to hold the particle against gravitational attraction, then a vertical force balance can be set up in terms of the charge $q$ and the mass $m$ of the particle:

$$qE_v = mg = \frac{\pi}{6} \rho g D^3,$$

where $\rho$ is the particle density and $D$ is the diameter of the particle, assumed to be spherical. Under most operating conditions, the particle Reynolds number $Re \ll 1$, so Stokes law applies (Davis et al., 1987), allowing the particle size to be related to the applied horizontal electric field $E_h$ in a particularly simple way. The relevant force balance in the horizontal direction is

$$qE_h = 3\pi \eta l u D,$$  (2)

where $\eta$ is the viscosity of the gas and $u$ is the local free-stream gas speed. Particle charge, obtained from Eq. (1), may be substituted into Eq. (2), from which the particle diameter may be determined as

$$D = \frac{3 \left( \frac{2 \eta l}{\rho g} \cdot \frac{E_v}{E_h} \right)^{1/2}}{3 \left( \frac{2 \eta l}{\rho g} \cdot \frac{E_v}{E_h} \right)^{3/2}}.$$  (3)

The particle mass and charge may then be calculated:

$$m = 9\pi \left( \frac{2}{\rho} \right)^{1/2} \left( \frac{\eta l}{g} \cdot \frac{E_v}{E_h} \right)^{3/2}$$  (4)

$$q = 9\pi \left[ \frac{2}{\rho g} \left( \eta l \right)^3 \right]^{1/2} \left( \frac{E_v}{E_h} \right)^{3/2}.$$  (5)
The cubic geometry of the cell, with its natural orthogonal control over the positioning of the particle, allows a set of useful relationships between particle size and charge to be derived and used in real time. Moreover, any influence of the drag force on the mass measurement, a concern in some prior experiments (e.g., Cohen et al., 1987a), is effectively absent with this configuration. The density of the particle is the only variable that needs to be obtained independently.

The electric fields needed for the calculation of mass and charge (Eqs. 4 and 5) occur at the center of the cell, yet only the voltages measured on the respective electrodes are typically available. As discussed by Sloane and Elmoursi (1989), these two quantities are related to each other via an empirically determined cell or balance constant $C_0$ to account for electrode geometry. Within a cubic cell the electric field tends to be understandably nonuniform near the corners and edges, where adjacent electrodes come into close proximity. However, near the center the field is relatively uniform and varies linearly with position about the null point (Allison and Kendall, 1996). Allison and Kendall have determined the cell constant to be 0.72 in each Cartesian direction via both theoretical calculation and experimental measurement in a three-dimensional electrolytic tank. Note that neither the determination of particle size (via Eq. 3) nor that of particle mass (via Eq. 4) are sensitive to the magnitude of $C_0$, for the cubic geometry because only the ratio of the fields in two directions is of importance. Only calculations of particle charge (via Eq. 5) are affected by the magnitude of $C_0$, in which case uncertainties in $C_0$ propagate linearly into uncertainties in $q$. The effects of the grid injector and other geometric asymmetries on the cell constant have not yet been explored.

The major uncertainties in the calculation of particle size, mass, or charge tend to arise from uncertainties in the freestream flow speed ($v$) in the center of the cell. Whereas the plug-flow approximation may be valid at the upstream face of the cell, the flow must develop to an uncertain extent toward a parabolic profile during passage through the cell. We have therefore used glass beads of sizes and densities traceable to the National Institute of Standards and Technology (NIST) in order to "calibrate" the flow. In effect, the well-defined Stokes drag on a known particle becomes our measure of the flow speed $v$ at any given reading of the mass flow meter in the relevant part of the external flow system. With this technique the uncertainty in $v$ is determined primarily by the standard deviation of the bead population used and currently amounts to about ±15%.

**Environmental Control**

The control of the gaseous environment surrounding the particle represents an important part of our ELS. The composite flow-control system that provides the required steady-state flows for our experimentation is shown schematically in Fig. 3. Once the clean and dry carrier gas is regulated to a manifold pressure of about 250 kPa, it is fed in parallel to the cell and grid-injector subsystems. The main flow is regulated by a mass flow controller ("MFC 1"; Tylan) configured with a bypass option. The bypass flow is regulated by MFC 2 before this flow enters the moisture source. The moist flow rejoins the main flow before the mixture enters the cell.

The reagent to be introduced through the grid injector is generated in the other subsystem, the one whose overall flow is controlled by MFC 3 in Fig. 3. For the experiments described here, we needed very low concentrations of nitric acid vapor, so this subsystem accommodated two stages of dilution. Very small flow rates of the carrier were fed into the reagent source through a manual fine-metering valve (Whitey) calibrated for prescribed pressure drops by a conventional soap-bubble technique. The source of nitric acid vapor was a liquid solution of 50% nitric acid (Baker Ulltrex II) and 50% sulfuric acid (Fisher Reagent Grade) contained in a temperature-controlled trap. The sulfuric acid was added to minimize the amount of water...
vapor picked up for any given vapor pressure of nitric acid and thereby to reduce the tendency for nitric acid vapor to stick to the walls of the flow system. The outflow from the reagent source was then selected, depending on the setting of the three-way valve, to pass into the grid or to bypass the cell altogether. The flow of the carrier into the grid injector, laden with reagent or not, was controlled by another fine-metering valve (Nupro) operated at prescribed pressure drops and calibrated as described above. The on–off valve at the exit of the grid injector determined the mode of injection: closed for “direct injection,” open for “parallel injection,” in which case the differential pressure between the grid and cell was controlled with the regulating valve in line with the vapor trap of the exhaust stream. As needed for a particular experiment, the effluent from the cell may be characterized (e.g., dew-point temperature, mass spectrometry) before it, too, is exhausted through the vapor trap.

The environment of the particle is also controllable in pressure and temperature. Pressure control is achieved for any given flow rate through the cell by changing the setting of the restriction valve just down-stream of the cell (see Fig. 3). As needed, this valve could be under computer control and the pressure in the cell servoed to simulate the pressure changes that atmospheric air parcels undergo during changes in elevation. The temperature of the cell is established by controlling the temperature setting of a refrigeration unit (Neslab ULT-95) containing a liquid coolant (Dow Siltherm XLT) that circulates in a jacket surrounding the cell. Between the temperature-control jacket and the cell itself are two air spaces separated by an aluminum
isolation chamber. The outer air space contains coils of stainless steel tubing used to precondition the temperature of the main and grid flows in a gradual and controlled way. The air inside the isolation chamber is circulated rapidly in order to refine the local temperature of the cell to the desired experimental values. The temperature of the gas in the cell is monitored with two thermocouples in the gas stream, one upstream of the flow straightener, the other downstream of the downstream electrode. The particle temperature is taken as the mean of the upstream and downstream gas temperatures. As with pressure, temperature can be ramped continuously up or down as needed by any given experiment.

Reagent Distribution

A particular advantage of the cubic-cell configuration lies in the fact that the cross sectional area of the cell remains uniform along the entire flow path. Thus, laminar flow is readily established by the upstream flow diffuser and maintained with minimal modification across the cell volume. The carrier gas can be laden with any component for which wall interactions pose little problem.

Reactive compounds or trace gases that interact strongly with the cell walls are introduced into the main flow via the grid injector shown in Fig. 2. These compounds are diluted with N₂ and introduced into the cell through a porous wall on the downstream side of each tube. Each of the six tubes opens into one of two stainless steel manifolds in alternating fashion, allowing two separate reagents to be introduced simultaneously. Each manifold is connected to the external gas-handling system through two tubes (not shown), so that either of two modes of gas introduction may be chosen. In the “direct-injection” mode, one of the connecting tubes to the manifold is sealed so that the flow through the porous injector walls is in series with the trace-gas flow brought in through the other tube. This is the arrangement used for the present series of experiments. However, when both connecting tubes to a given manifold are used, one may pass a relatively high flow of the trace gas and carrier through the manifold, allowing only a small portion of the mixture to enter the cell, as controlled by the differential pressure between the manifold and the cell. This “parallel-injection” mode is more complicated to control properly, but it offers advantages for rapidly changing the mixing ratios of reagents in the cell, such as may be needed for studies of some kinetic phenomena (e.g., Foss and Davis, 1994).

The introduction of reactive gases immediately upstream of the levitated particle offers advantages for some types of experimentation as long as care is taken during the design and use of the grid injector. In principle, a single upstream orifice could be used to introduce the trace gas into a laminar background flow, but the concentration of reagent in the gas stream would be a strong function of position within the cell due to the diffusion-limited mixing of the reagent into the main-flow gas. Knowledge of the reagent mixing ratio at the exact location of the particle would thus be uncertain. The employment of several line sources, as in the present grid-injection concept, permits the reagent mixing ratio to be made relatively uniform across the cell.

The multiple injection of reagent serves to distribute the trace component uniformly across the cell whenever the spacing between the injectors is small relative to the cross-flow dimension of the cell. With reference to the top view of the cell given in Fig. 4, consider the steady and uniform inflow of reagent into the main flow along the length of each injection tube and its impact on the distribution of reagent within the cell. The injection tubes are evenly spaced with a distance Δg between the center lines, whereas the inside dimension of the cell is L_{cell}. The background flow is assumed to be uniform and laminar with speed u, and the reagent diffusion coefficient is D_r. In this analysis we ignore any possible microturbulence that may be set.
up in the wakes of the injection tubes and assume that all mixing occurs strictly by molecular diffusion, a worst-case scenario. The “boundaries” of the various reagent plumes, shown schematically in Fig. 4, are seen to overlap at a distance $L_D$ downstream of the grid once the mean cross-flow displacement $y = \Delta_G / 2$. Thus, upon simultaneous consideration of the advective flow and the Einsteinian relationship for diffusion (Atkins, 1986, p. 680), we take $L_D$ to be an approximate measure of the minimum distance beyond which the reagent can be considered to be uniformly mixed across the cell flow. The magnitude of $L_D$ in our system, when $v = 1 \text{ cm s}^{-1}$ and $D_v = 0.1 \text{ cm}^2 \text{ s}^{-1}$, is 0.2 cm. The uncertainty in the reagent mixing ratio is thus minimized near any test particle situated downstream of this distance.

The degree of uniformity of the reagent mixing ratio at any given location downstream of the injector plane can be estimated by solving the convective-diffusion equation (Probstein, 1994, p. 41). For this application it suffices to treat each of the six injectors as an independent steady point source of reagent in a given horizontal plane (as depicted in Fig. 4) and consider only the transverse component of diffusion. The result of this analysis is presented in Fig. 5 for the case of $L_D = 0.2 \text{ cm}$. Each panel of the figure shows the relative concentration of reagent as a function of the cross-flow position ($y$) at the specified downstream distance ($x$). The net concentration (bold curve) is the sum of the individual contributions from all of the injector tubes, shown by the thin curves. Near the injector plane (e.g., $x = 0.1 \text{ cm}$, lower panel of Fig. 5) the concentration varies periodically with $y$ under the strong influence of the closest reagent source. Further downstream, however, the contributions from neighboring reagent sources become progressively more important, and the net concentration becomes more uniform. In the plane located at $x = L_D = 0.2 \text{ cm}$ (middle panel of the figure), the concentration is nearly uniform across the cell flow.

FIGURE 4. A top view of the cell, schematically showing the diffusion of reagent into the background flow of carrier gas (entering from the right). Note that the test particle is located in a region of relatively uniform reagent concentration, but outside of the zone influenced by the cell walls.
of Fig. 5), the reagent concentration varies only \( \pm 1.4\% \) about the mean in the central region.

The influence of the cell walls must also be considered in this analysis because some of the injection tubes lie near those surfaces. Products of heterogeneous reactions occurring on the walls could conceivably enter the gas stream and diffuse to the test particle, where unwanted influences on the processes being studied could be felt. This negative effect of the walls could materialize if the particle position \( x_p \) satisfies the criterion \( L_D < x_p < L_w \). This situation is readily met whenever \( L_D/L_w \ll 1 \). For given flow speed and diffusion coefficient, the scales for diffusive mixing \( L_D \) and wall interactions \( L_w \) are related to the physical parameters of the cell by

\[
\frac{L_D}{L_w} = \left( \frac{\Delta_G}{L_{cell}} \right)^2,
\]

so it is generally sufficient to ensure that \( \Delta_G \ll L_{cell} \). While the details of flow gradients and diffusion near the walls would need to be taken into account in a rigorous analysis, the conclusion still prevails that the distributed introduction of reagent just upstream of the particle provides a convenient means for ensuring uniform and known reagent mixing ratios near the center of a cubic cell, while at the same time avoiding unwanted influences from the walls.

**Experimental Procedures**

Experiments start with the launching of a chosen type of particle into the cell. Solid particles, such as salts or glass beads, are first inserted as a fine powder into a small metal cylinder that has a small hole in its flat bottom surface. A loose-fitting plunger, serving both as a lid to contain the powder and as an electrode, is then inserted into the cylinder. As a high voltage is suddenly applied to the plunger, several particles are ejected from the cylinder through the hole in the base. These charged particles are allowed to fall through a hole in the top electrode and into the center region of the cell, where a few of them are trapped by
the electrodynamic field. Via manipulation of the DC voltages on the cell electrodes all but one of the particles can be rejected. Liquid particles are similarly launched and selected, except that the launcher consists of a fine glass tube affixed to a fitting (Swagelok) that serves as the liquid reservoir. Tiny droplets are mechanically ejected through a small hole in the tip of the glass tube when the top of the fitting (made into a tight-fitting plunger) is gently tapped. The ejected droplets acquire a net charge when a high voltage is applied to a metal cylinder that surrounds the glass tip and grounded liquid.

The experimental procedure followed once a particle is isolated and trapped at the electrical center of the cell varies with the goals of the investigation. In our study of aqueous particles we have been particularly interested in measuring the mass growth of the particles as the saturation ratios of water and nitric acid vapors in the environmental gas increase. A recently introduced particle was therefore allowed to equilibrate with a clean gas at relatively low humidities for some time before actual experimentation began. Especially when using sulfuric acid droplets, we have found it necessary to let the system dry out for several hours, sometimes overnight, due to the very hygroscopic nature of concentrated sulfuric acid and its tendency to respond sensitively to minute concentrations of water vapor. During this initial conditioning time, the AC voltages were kept fairly high (~1 kV) in order to ensure that the unattended particle was not lost. This time was also used to set up the computer control and tracking of the DC voltages used to maintain the particle in the center of the cell.

The mass growth of salt and sulfuric acid particles was measured in our experiments by incrementally increasing (alternatively decreasing) the relative humidity for fixed nitric acid mixing ratios. The flows of N₂ through the cell and grid injector were held fixed at 5 and 0.5 cm³ s⁻¹, respectively, while the flow through the humidifier was changed systematically (between 0 and 5 cm³ s⁻¹). Except when nitric acid was included in the gaseous mixture, the dewpoint temperature of the cell effluent was monitored directly with a chilled-mirror hygrometer (General Eastern Hygro-M2). Otherwise, the relative humidity was computed from the calibrated flow rates into the cell. The nitric acid mixing ratio was similarly computed from the flows under the assumption that the gas flowing through the vapor source became saturated. Relative humidities were calculated, as were the nitric acid saturation ratios, as the ratio of the respective partial pressures to the equilibrium vapor pressure of the pure component at the temperature of the cell. The "relative mass" was directly measured as the ratio of the vertical DC voltages needed to center the particle under moist and completely dry conditions, respectively.

RESULTS AND DISCUSSION

Representative results obtained at room temperature and atmospheric pressure are presented here to demonstrate the capabilities of the experimental system described above. The deliquescence growth of a pure salt (NaNO₃) is shown in Fig. 6. The relative mass (m/m₀) of the particle is seen to remain constant as the relative humidity (RH) is increased from low values to slightly greater than 70%. Then, as is characteristic

![FIGURE 6. Measurements of the relative mass (m/m₀) of a sodium nitrate particle and its dependence on relative humidity. Arrows indicate the direction of the applied change in humidity. The dry diameter (D_{dry}) of the particle was determined as described in the text.](image)
of pure salts, the particle mass rapidly increased with increasing values of RH. The deliquescence point obtained in these experimental runs agrees well with that found by others for this salt (e.g., Tang and Munkelwitz, 1993). Beyond the deliquescence relative humidity the particle grew in mass with a trend that increasingly approximated that due to Raoult’s law (Pruppacher and Klett, 1978, p. 80). The particle used in this experiment was large (20 \mu m dry diameter), so we should not expect any effects of drop curvature to show up in the data. As the applied humidity was lowered, we observed the classic hysteresis behavior (shown by the arrows in Fig. 6) and recrystallization of the salt at RH values below about 40%. This same experimental technique can be used equally well to characterize the deliquescence and efflorescence of more complicated aerosol systems. In the case of multicomponent salts, for instance, one would expect the deliquescence points to occur at RH values lower than those of any of the single salts because of the tendency for the solid phases to dissolve at the eutectic point of the mixture (Wexler and Seinfeld, 1991; Tang and Munkelwitz, 1993).

During other experiments salt particles were levitated to measure their Raman spectra. The observed Raman shifts are in excellent agreement with values available in the literature (Fung and Tang, 1988). In each spectrum of Fig. 7, the strongest peak represents Raman scatter due to the symmetric stretching mode of the N–O or S–O bonds in the respective anion group. As seen in Fig. 7a, a distinct change in the magnitude of the Raman shift and a change in the shape of the peak arising from the NO$_3^-$ ion is evident upon uptake of water. The NaNO$_3$ solution drop shows the Raman shift that is characteristic of the free NO$_3^-$ anion (Tang and Fung, 1989). The Raman spectrum of the particles also characterizes the chemical composition of the salt, as shown in Fig. 7b. The two minor sharp lines (between 1000 and 1100 cm$^{-1}$) in each panel are “plasma lines” present in the unfiltered output of the laser and elastically scattered by the particle. In this case
the plasma lines are the relatively strong 514.2 and 514.5 nm transitions of Ar, which appear as "Raman shifts" of 1044 cm⁻¹ and 1057 cm⁻¹, respectively, relative to the 488 nm line. Thus they appear close to the nitrate feature (at 1067 cm⁻¹) of the NaNO₃ salt particle, but above the sulfate feature (at 996 cm⁻¹) of the Na₂SO₄ particle. One advantage of the cubic cell for Raman spectroscopy is of course the relatively large, flat windows that can be used for gathering low-intensity light over large solid angles.

Sulfuric acid represents another interesting substance for investigation in a single-particle levitator. The results from a number of experiments using several different sulfuric acid particles are shown in Fig. 8. In contrast with salts, sulfuric acid exhibits no deliquescence point and stays liquid at all humidities. For the same reason, sulfuric acid particles grow and evaporate without any hysteresis effects. The particle mass data from our experiments show very good agreement with theory (solid curve) based on the bulk thermodynamic data compiled by Zeleznik (1991).

When sulfuric acid is exposed to both nitric acid and water vapor simultaneously, the particle growth becomes more complicated. Figure 9 shows new results obtained from our particle mass measurements when various fixed fluxes of nitric acid vapor were introduced into the cell through three of the six grid injector tubes. The bold curve shown here is the same as the theoretical curve of Fig. 8 and is used as reference for the case when no nitric acid was present in the system. As the relative humidity was increased from low values we saw little change at first from the particle growth measured with pure sulfuric acid solutions. However, at higher RH the effect of the nitric acid became progressively more apparent. The ternary solution drop grew large even under strongly subsaturated conditions when the nitric acid saturation ratio (Sₐ) was appreciable (values approaching 10⁻²). Part of this additional growth was obviously due to the absorption of nitric acid, but additional water must also have been taken up as a consequence of the lowering of the water activity by the additional solute in the liquid phase. Measure-

![Figure 8](image-url)
ments such as these that depend on the quantitative addition of a reactive compound to the gas phase benefit greatly from an apparatus that introduces a trace gas uniformly in a wall-less mode.

These experimental findings agree very well with the theory (thin curves in Fig. 9) derived from bulk thermodynamic data near room temperature (Jaecker-Voirol et al., 1990) when $S_n$ is used as a fitting parameter. The magnitudes of $S_n$ used to achieve a good fit to the data differ from the values calculated from the experimental flow rates by about 25%. Under the assumption that the literature data are correct, the difference could be accounted for by some laser heating of the particle or incomplete mixing in the cell. Only additional investigations can resolve the cause of this discrepancy. As with the salt particles, all of the droplets in these experiments were relatively large (diameters between about 5 and 20 μm), so the effects of curvature do not show up in the data.

Given the reasonable agreement found between the particle data and theory for ternary solution drops, we can exploit the internal relationships upon which the theory is based. In particular, we make use of the fact that the theory of Jaecker-Voirol et al. (1990) establishes a unique relationship between the weight fraction of the various components in the solution phase and the partial pressures of each component in the vapor phase. Through iterative solutions of their equations we calculated the particle composition needed to yield the experimentally imposed saturation ratios of water and nitric acid in the vapor phase. These results are shown in Fig. 10 for three representative values of $S_n$. Here, the weight percent of each component, sulfuric acid, nitric acid, and water, is plotted as an implicit function of RH for each value of $S_n$. At very low relative humidities, a typical particle is composed mostly of sulfuric acid, and the three curves overlap one another in the composition region in which the solubility of nitric acid is small, probably as a consequence of the low degree of HNO$_3$ dissociation (Van Doren et al., 1991). As the RH increases in the gas about the particle (and the loci of points move toward the right in Fig. 10, as shown by the arrows), the solution gradually becomes more dilute, allowing some nitric
FIGURE 10. A ternary diagram for the sulfuric acid–nitric acid–water system. The solid curves show the loci of points indicating the composition of a particle in equilibrium with steadily increasing humidities (direction shown by the arrows) at the indicated fixed nitric acid saturation ratios.

The relatively profound influence that even low levels of nitric acid vapor have on the growth of aqueous particles at modest relative humidities has interesting consequences for atmospheric aerosols. The main point to note is that the effect of nitric acid vapor on the water activity differs qualitatively, as well as quantitatively from that of a nonvolatile solute like sulfuric acid. The effect of nonvolatile solutes on the mass growth of atmospheric particles has been extensively studied (Pruppacher and Klett, 1978, p. 141; Tang and Munkelwitz, 1993), but the effects of volatile components have been little explored. Whereas a nonvolatile solute necessarily becomes progressively diluted (and inactive) as a particle grows by the uptake of water, a volatile solute tends to maintain a fixed activity during particle growth. Thus, as an aqueous particle grows in volume, additional solute is continually absorbed from the environment, until of course significant depletion of that constituent from the gas phase occurs. Nitric acid, in particular, is a highly soluble, but nevertheless volatile compound in dilute aqueous solutions that can profoundly lower the water activity at high RH, when otherwise the effects of the nonvolatile solute are minimal. As we can see from the strong upward trends of particle mass with increasing RH in Fig. 9, bulk condensation occurs at RH values well below 100% when the nitric acid saturation ratio exceeds about $10^{-5}$. Such nitric acid saturation ratios are just barely attained in moderately polluted urban environments (Spicer, 1982), but at lower temperatures, such as those found in the Arctic troposphere or in the stratosphere, the ambient values of $S_n$ are likely to increase by one to two orders of magnitude. The implications of such behavior on cloud formation have been explored theoretically (Lamb, 1992; Kulmala et al., 1993; Carslaw et al., 1994), but to our knowledge the direct measurement of the enhanced mass growth of aqueous particles due to the presence of nitric acid vapor has not been made before. In general, we expect that haze and cloud formation is stimulated in the atmosphere whenever suitably large saturation ratios of a soluble trace gas are present.

SUMMARY AND CONCLUSIONS

In this paper we have described a new experimental system for investigating the properties and behavior of individual aerosol particles under controlled environmental conditions. The particles were levi-
Electrodynamic Levitator for Liquid Droplets

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Cubic Electrodynamic Levitator for Liquid Droplets

In a cubic cell, the walls of which served both as electrodes and as pressure- and flow-containment surfaces. A two-phase AC voltage source was applied to the vertically oriented faces to achieve a time-averaged restoring force, while DC voltages applied to all faces permitted simple and robust three-axis positioning of the particle within the cell volume. The gaseous environment of the particle was readily controlled in composition, pressure and temperature with this geometry because of the ease with which a lateral flow of gas can be made to pass through the cell. Rather than serving as an interference to the particle mass measurement, this flow induces a well-defined drag force on the particle that can be exploited to determine the mass and charge of the particle in absolute units. Reactive reagents are introduced in a quantitative way just upstream of the particle through an injector grid that also serves as one of the electrodes. Such a distributed introduction of reagent into a cell of uniform cross-section makes the system serve as a wall-less flow reactor that is suitable for numerous equilibrium and kinetic studies of isolated aerosol particles.

Preliminary experiments were performed with this system to demonstrate its usefulness in the study of aerosol particles exposed to water vapor and volatile solutes. Fundamental distinctions between the mass growth of salt and sulfuric acid particles were readily observed. Sulfuric acid particles exposed simultaneously to the vapors of water and nitric acid experienced enhanced growths in mass that can be explained through application of the thermodynamics of bulk ternary solutions. These new data show that a qualitative distinction exists between the effects of nonvolatile and volatile solutes on the size of aqueous particles at various relative humidities, behavior that is expected to show up in the atmosphere in low-temperature environments of modest nitric acid mixing ratios during haze and cloud formation.

Future work with this levitation concept will focus on improvements in the apparatus itself, as well as on experiments with a broader range of gas-particle systems. We are currently expanding the capabilities for chemically characterizing the gas-phase constituents. A quadrupole mass spectrometer (Extrel) is being outfitted with an atmospheric-pressure ionization inlet for interfacing to the cell effluent with minimal wall losses. We also plan to measure the elastic-scattering properties of the levitated particle so as to gain independent size information and infer values of particle density and refractive index. New experiments with sulfuric acid particles exposed to water and nitric acid vapors will take place at low temperatures (those approaching 190 K) in order to verify theoretical ternary solution models and investigate possible changes of particle phase. Smaller particles will be used so that the effect of curvature (and therefore surface tension) on the particle size can be introduced, thereby providing a unique set of particle-oriented measurements of direct relevance to the formation of polar stratospheric clouds.

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