

Aerosol Losses in a 100 L Tedlar® Bag

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Abstract

Aerosol losses in a 100 L Tedlar® bag were investigated for the aerosols with number median diameter of 0.05 μm and number concentration of $6.4 \times 10^4 \text{ cm}^{-3}$. Over a 1 hr period, loss of particles in the bag is apparent, and the volume decrease with time is significant. The number concentration, surface area, and volume concentration of the aerosols decreased to 34, 50, and 52% of the initial value in 30 min, respectively. This indicates that deposition to the walls was the main loss process for aerosols in the Tedlar® bag. Theoretical calculations showed that coagulations and deposition by diffusion and gravitational sedimentation would not change aerosol characteristics significantly, and the electrical force was the dominant loss process for particles in the Tedlar® bag over a 1 hr period.

Key words : Smog chambers, Aerosol losses, Tedlar® bags, Electrical forces

1. INTRODUCTION

The troposphere is a heterogeneous system that consists of gaseous species and aerosols. Thus, understanding the role of aerosols on various gas-phase reactions in the troposphere is critical to accurate predictions of the atmospheric pollutant levels, including their formation and decay. However, effects of aerosols on gas-phase reactions have not been adequately investigated (Warneck *et al.*, 1996). Recently, heterogeneous kinetics in the troposphere has received increased attentions (Oh and Andino, 2000; Behnke *et al.*, 1988). Thus, the proper experimental methods studying heterogeneous kinetics pertinent to the troposphere are required. Smog (or environmental) chambers are widely used to study

the atmospheric chemical processes (Finlayson-Pitts and Pitts, 2000), and also the most candidate tool for heterogeneous kinetic studies. Smog chambers are made from glass, Teflon® or Tedlar® films that are chemically inert. However, once aerosols with a specific characteristic are introduced to a smog chamber, they are subject to change their concentration and size distribution in a relatively short time period due to various dynamic processes including coagulation, diffusion, electrical motion, and sedimentation. A change in aerosol characteristics during an experiment can significantly affect the reaction kinetics. Thus, understanding aerosol dynamics and controlling aerosol characteristics in a smog chamber are essential to studying heterogeneous kinetics adequately.

The purpose of this study is to understand aerosol dynamics in a 100 L Tedlar® bag, and determine the time interval that allow to conduct heterogeneous

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kinetic studies without severe changes in aerosol characteristics.

2. EXPERIMENTAL METHODS

Experiments were carried out in one hundred liter, 2-mil Tedlar® bags (SKC Inc., 231-50, 76 cm × 91 cm). Tedlar® bags are widely used for air samplings and laboratory studies for gas-phase reactions pertinent to the tropospheric processes. A schematic of the experimental system appears in Figure 1. The aerosol was generated by using a Collision atomizer to atomize an aqueous solution containing ammonium sulfate. The atomization of solutions with compressed air is one of the simplest ways to generate a polydispersed aerosol. The aerosol generated was passed through a diffusional dryer and a ⁸⁵Kr charge neutralizer (TSI Inc., Model 3012) before being introduced to the bag. In the charge neutralizer, a charge equilibrium called Boltzmann equilibrium is reached where the aerosol carries a bipolar distribution (Hinds, 1982). The aerosol concentration in the bag was controlled by changing the amount of aerosol flow into the bag. The phases of the aerosols used in this study were likely solid, since the relative humidity of air in the system was approximately 20%, values that are below the efflorescence (recrystallization) relative humidity of the aerosols studied. The efflorescence relative humidity of (NH₄)₂SO₄ is 40% (Seinfeld & Pandis 1998). After admitting aerosols in the bag, aerosol size

distributions were measured at different times. The number size distribution of the particles in the Tedlar® bag was determined using an electrical aerosol analyzer (EAA, Model 3030, TSI, Inc). These data were converted from number distribution to surface area and volume distributions assuming spherically shaped particles. The initial aerosol number median diameter and number concentration were approximately 0.05 μm and 6.4 × 10⁴ cm⁻³, respectively. These corresponded to a surface area median diameter, surface area, mass median diameter, and mass concentration of approximately 0.15 μm, 1,400 μm² cm⁻³, 0.20 μm, and 62 μg m⁻³, respectively. These values are in the range of atmospheric aerosols for polluted urban areas (Hughes *et al.*, 1998). The initial size distributions of aerosols tested in this study are shown in Figure 2.

3. RESULTS AND DISCUSSION

3.1 Theoretical considerations

To estimate the optimal aerosol conditions at which the changes in aerosol characteristics were minimized, a simple calculation was conducted assuming the existence of monodisperse particles. It is important to note that the particles generated from the collision atomizer were polydispersed. However, the calculated results for the monodisperse particles provide a general guide. Particles in a chamber interact with the walls as well as other particles to change their size distribution and concentration. Coagulation and deposition on the walls are the most dominant aerosol loss processes in a chamber (Crump and Seinfeld, 1981). These processes are governed by several factors such as diffusion (thermal force), gravity, and electrical forces. Coagulation is a process that involves particle collision due to the relative motion between particles and subsequent adhesion to form larger particles. The net result is a decrease in number concentration and an increase in particle size. Thus, coagulation of particles causes a decrease in number concentration and surface area. However, the mass (volume) concentration remains constant during the coagulation pro-

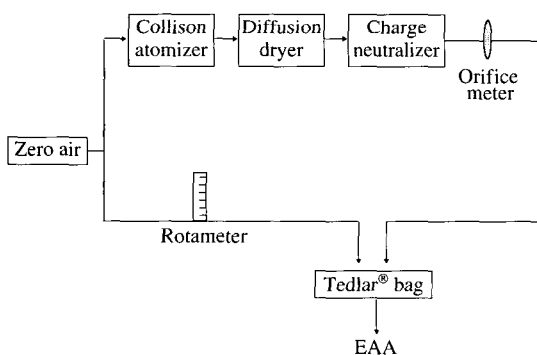


Fig. 1. Schematic of the experimental apparatus.

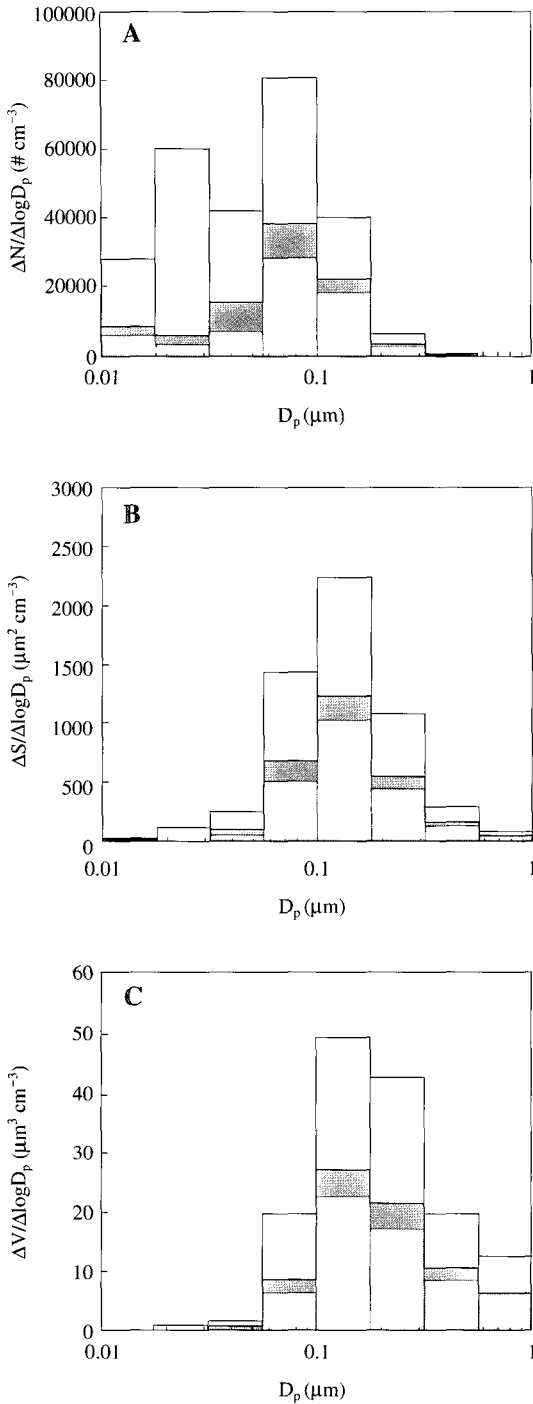


Fig. 2. Size distributions of the aerosols in the bag at different times; initially (\square), after 30 min (\square), and after 60 min (\cdot). (A) Number (B) Surface Area (C) Volume.

cess. Coagulation is a spontaneous and ever-present phenomenon for aerosols due to the Brownian motion of particles. The coagulation rate of mono-disperse particles undergoing Brownian motion depends on the number concentration, size, and diffusion coefficient of the particles. The rate is represented by the following equation (Hinds, 1982):

$$\frac{dN}{dt} = -KN^2 \tag{1}$$

$$K = 4\pi D_p D \tag{2}$$

where N is the number concentration, K is the coagulation coefficient, D_p is the particle diameter, and D is the diffusion coefficient of the particle. The number concentration as a function of time can be obtained by integrating equation (1) assuming K to be constant:

$$N(t) = \frac{N_o}{1 + N_o K t} \tag{3}$$

where N_o is the original number concentration at time zero and $N(t)$ is the number concentration at time t . Also, the following relationship is applicable since the particulate mass concentration (C_m) remains constant during coagulation (assuming liquid particles):

$$C_m = N_o \frac{\pi}{6} \rho_p D_o^3 = N(t) \frac{\pi}{6} \rho_p (D_p(t))^3 \tag{4}$$

where D_o is the initial particle size, $D_p(t)$ is the particle size at time t , and ρ_p is the density of the particle. Rearranging equation (4) and substituting equation (3) gives the following relationships for particle size changes during coagulation:

$$D(t) = D_o \left(\frac{N_o}{N(t)} \right)^{\frac{1}{3}} = D_o (1 + N_o K t)^{\frac{1}{3}} \tag{5}$$

By analogy, the total surface area of aerosols can be represented by the following equations:

$$\frac{S(t)}{S_o} = \frac{N(t) \pi (D_p(t))^2}{N_o \pi D_o^2} = \frac{1}{(1 + N_o K t)^{\frac{2}{3}}} \tag{6}$$

$$\text{or } S(t) = \frac{S_o}{(1 + N_o K t)^{\frac{2}{3}}} \tag{6a}$$

where S_o is the initial total surface area, and $S(t)$

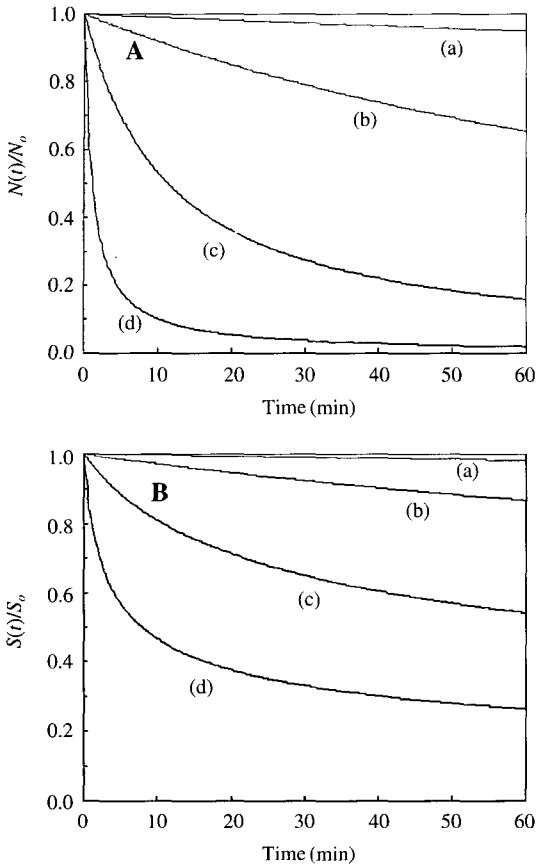


Fig. 3. Normalized number concentrations of particles as a function of time due to coagulation for monodisperse particles with diameters of 0.05 μm at initial concentrations of (a) 10⁴, (b) 10⁵, (c) 10⁶, and (d) 10⁷ cm⁻³. Plot (A) represents number concentration and plot (B) represents total surface area.

is the total surface area of particles at time t . Using equations (3) and (6a), changes in the aerosol number concentration and total surface area were calculated for monodisperse particles with a diameter of 0.05 μm and at different initial concentrations ($N_0 = 10^4, 10^5, 10^6, 10^7$ cm⁻³). The particle diameter of 0.05 μm was chosen since the median number diameter of the aerosols tested in this study was 0.05 μm. A diffusion coefficient (D) of 2.37×10^{-5} cm² s⁻¹ was used. Plots of $N(t)/N_0$ and $S(t)/S_0$ over a 1 hr period are shown in Figure 3. This figure clearly illustrates the profound effect that coagulation has on both number concentration and surface area over time as a function of initial concentration. For initial concentrations of 10⁴, 10⁵, 10⁶, and 10⁷ cm⁻³, the values of $N(t)/N_0$ after 1 hr were 0.95, 0.65, 0.16, and 0.02, respectively. The corresponding values of $S(t)/S_0$ were 0.98, 0.87, 0.54, and 0.27. A decrease in the surface area of more than 46% of the initial value is realized after 1 hr when the initial concentration is larger than 10⁶ cm⁻³. Thus, to minimize the effects of coagulation over short time periods in a chamber, the initial aerosol number concentration should be less than 10⁵ cm⁻³. Since the initial aerosol number concentration was 6.43×10^4 cm⁻³ in this study, changes in aerosol characteristics by coagulation over a 1 hr period was not expected to be the major loss process in the bag. To estimate the changes in aerosol characteristics for different sizes of particles by coagulation, the values of $N(t)/N_0$ after 1 hr were calculated for particles with diameters of 0.01, 0.1, 0.5, 1, 5, and 10 μm. As shown in

Table 1. Normalized number concentrations of particles over a 1 hr period ($N(t)/N_0$) due to coagulation for monodisperse particles at different initial aerosol concentrations.

D_p (μm)	D^a (cm ² s ⁻¹)	K^b (cm ³ s ⁻¹)	$N(t)/N_0$			
			$N_0=10^4$ cm ⁻³	$N_0=10^5$ cm ⁻³	$N_0=10^6$ cm ⁻³	$N_0=10^7$ cm ⁻³
0.01	5.23×10^{-4}	6.57×10^{-9}	0.81	0.30	0.04	0.00
0.05	2.37×10^{-5}	1.49×10^{-9}	0.95	0.65	0.16	0.02
0.1	6.75×10^{-6}	8.48×10^{-10}	0.97	0.77	0.25	0.03
0.5	6.26×10^{-7}	3.93×10^{-10}	0.99	0.88	0.41	0.07
1	2.74×10^{-7}	3.44×10^{-10}	0.99	0.89	0.45	0.07
5	4.86×10^{-8}	3.05×10^{-10}	0.99	0.90	0.48	0.08
10	2.39×10^{-8}	3.00×10^{-10}	0.99	0.90	0.48	0.08

^aDiffusion coefficients

^bCoagulation coefficients

Table 1, decreases in number concentration of monodisperse aerosols by coagulation were increased as increases in particle diameters. However, particles with diameters larger than 0.5 μm showed the similar values of $N(t)/N_o$, since coagulation coefficients of particles were nearly constant.

The loss of particles by deposition on the walls is inevitable since particles adhere when they collide with a surface. Deposition is due to Brownian and turbulent diffusion, gravitational sedimentation, and electrostatic forces (McMurry and Rader, 1985), and results in decreases in number, surface, and volume concentrations. To estimate the loss of particles by deposition in a Tedlar® bag, the loss rates of each process was calculated for monodisperse particles with diameters of 0.05 μm in a 100 liter cylindrically shaped bag ($r = 19$ cm, $H = 91$ cm). The bag was assumed to be cylindrically shaped since the characteristic dimensions of the bag can be properly defined. Diffusion is generally the dominant force for smaller particles (less than 0.1 μm). The cumulative number of particles deposited per unit area of surface by diffusion, $n(t)$ in with units of number of particles per cm², is expressed by the following equation assuming a uniform concentration (N_o , with units of number of particles per cm³) in the bulk phase (Hinds, 1982):

$$n(t) = 2N_o \left(\frac{Dt}{\pi} \right)^{1/2} \tag{7}$$

where D is the diffusion coefficient, and t is the time. Assuming that deposition due to diffusion is the only loss process in the bag, the following balance equation holds:

$$N_o V = N(t)V + n(t)S \tag{8}$$

where S is the total surface area and V is the total volume of the container. Rearranging equation (8) gives the following relationship for the number concentration of aerosols as a function of time:

$$N(t) = N_o - n(t) \left(\frac{S}{V} \right) = N_o \left(1 - 2 \left(\frac{Dt}{\pi} \right)^{1/2} \left(\frac{S}{V} \right) \right) \tag{9}$$

Equation (9) shows that deposition by diffusion depends on the shape of the container (S/V) as well

as the diffusion coefficient of the particle (D). The loss of particles by gravitational sedimentation depends on the terminal settling velocity of the particle (V_{TS}) and the height (H) of the container. The number concentration of aerosols as a function of time due to gravitational sedimentation is expressed by the following equation assuming a uniform particle concentration in the container (Hinds, 1982):

$$N(t) = N_o \exp \left(\frac{-V_{TS}t}{H} \right) \tag{10}$$

The terminal settling velocity of particles (V_{TS}) with diameters less than 10 μm (Reynolds number $< 2 \times 10^{-3}$) is expressed by the Stokes-Cunningham law:

$$V_{TS} = \frac{\rho_p D_p^2 g C_c}{18 \eta} \tag{11}$$

where g is the acceleration gravity, C_c is the Cunningham correction factor, and η is the viscosity of air. Gravity is generally the dominant force for particles larger than 1.0 μm. Changes in number concentrations of aerosols due to deposition by diffusion and gravitational sedimentation for monodisperse particles with diameters of 0.05 μm in a 100 liter cylindrically shaped bag were calculated using equations (9) and (10). Estimated particle losses by gravitational sedimentation were negligible (less than 0.1% of the initial particle number concentration) if a 1 hr time period was considered. Deposition by diffusion was the dominant deposition process under the conditions used. However, only 5% of the initial particle number was determined to deposit to the surface under a 1 hr period. Thus, particle losses by diffusion and gravitational sedimentation were not expected to change aerosol characteristics significantly in a Tedlar® bag over a 1 hr period. The calculated $N(t)/N_o$ values are listed in Table 2.

The electrical force is an important factor for aerosol dynamics in a Teflon® chamber, since the surfaces of Teflon® (polytetrafluoroethylene) films are quite electrostatic (McMurry and Radar, 1985). McMurry and Radar (1985) showed that particles in the 0.05 to 1 μm size range were removed in a 250

Table 2. Normalized number concentrations of particles as a function of time ($N(t)/N_o$) due to deposition losses for monodisperse particles with diameters of $0.05 \mu\text{m}$ in a 100 liter cylindrically shaped bag. Losses are in parentheses.

Time (min)	$N(t)/N_o$			
	Diffusion	Gravitational sedimentation	Electrical force ^a	Total losses ^b
15	0.978 (0.022)	1.000 (0.000)	0.609 (0.391)	0.588 (0.413)
30	0.970 (0.030)	0.999 (0.001)	0.602 (0.398)	0.571 (0.429)
45	0.963 (0.037)	0.999 (0.001)	0.602 (0.398)	0.564 (0.436)
60	0.957 (0.043)	0.999 (0.001)	0.602 (0.398)	0.558 (0.442)

^aValues for particles carrying charges with Boltzmann equilibrium in an electric field of 45 volts/cm

^bObtained by adding the losses due to each process using the following formula:

$$\left(\frac{N(t)}{N_o}\right)_{\text{Total}} = 1 - \sum \left(1 - \frac{N(t)}{N_o}\right)_{\text{deposition process}}$$

liter Teflon[®] chamber primarily by electrostatic attraction to the Teflon[®] surfaces. A characteristic value of 45 volts/cm was found as the electric field intensity (McMurry and Radar, 1985). Since Tedlar[®] (polyvinylflouride) has a chemical structure similar to Teflon[®], the surfaces of Tedlar[®] films are very likely electrostatic, and the aerosol dynamics in a Tedlar[®] bag are likely influenced by electrical forces. As described earlier in the experimental description section, aerosols in this study carried charges with Boltzmann distribution since the generated aerosols passed through a charge neutralizer before being admitted to the Tedlar[®] bag. The charge distributions depend on the size of particle and particles carry more charge as their sizes increase. When a charged particle is placed in an electric field, it experiences an electrical force that ultimately influences the particle's velocity, V_{TE} . Mathematically, the velocity of particles with diameters less than $10 \mu\text{m}$ is expressed as (Hinds, 1982):

$$V_{TE} = \frac{neEC_c}{3\pi\eta D_p} \quad (12)$$

where n is the number charge acquired by a particle, e is the elementary unit of charge, and E is the electric field intensity. The number concentration of aerosols as a function of time as a result of

deposition due to electrical forces in a cylindrically shaped container having an electric field in a horizontal direction is

$$N(t) = N_o \exp\left(\frac{-2V_{TE}t}{r}\right) \quad (13)$$

where r is the cross-sectional radius of the container. Changes in number concentrations of aerosols due to electrical deposition for monodisperse particles with diameters of $0.05 \mu\text{m}$ in a 100 liter cylindrically shaped bag were calculated using equation (13). An electric field intensity of 45 volts/cm was assumed, and the $N(t)/N_o$ values obtained are listed in Table 2. Since most of the charged $0.05 \mu\text{m}$ sized particles are singly charged (Hinds, 1982), the calculation was performed only for singly charge particles. Estimated losses due to electrical deposition were significant; 98% of the singly charged particles were estimated to deposit to the surface within a 15 min period. Since approximately 40% of $0.05 \mu\text{m}$ -sized particles are singly charged at the Boltzmann equilibrium condition, 39% of the initial particle number was determined to deposit due to electrical forces within a 15 min period. Neutral particles were assumed not to deposit as a result of electrical forces. Thus, particle loss by electrical deposition was expected to change aerosol characteristics significantly in a Tedlar[®] bag over a 1 hr period.

The number concentration of aerosols as a function of time as a result of all deposition processes was obtained by adding the losses due to each process using the following equation.

$$\left(\frac{N(t)}{N_o}\right)_{\text{Total}} = 1 - \sum \left(1 - \frac{N(t)}{N_o}\right)_{\text{deposition process}} \quad (14)$$

The $N(t)/N_o$ values obtained are listed in Table 1, and plots of $N(t)/N_o$ are shown in Figure 4. The total losses by deposition for monodisperse particles with diameters of $0.05 \mu\text{m}$ in a 100 liter cylindrically shaped bag were significant in a 1 hr period. The estimated $N(t)/N_o$ value was 0.558, indicating that approximately 44% of the initial particles were lost as a result of deposition over a 1 hr period. Even though the calculation is based on monodisperse particles and a cylindrically shaped bag, the results

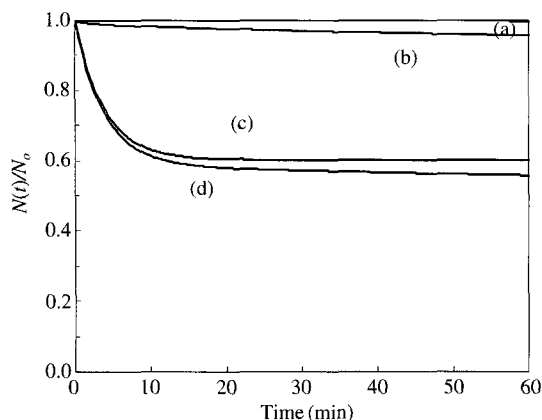


Fig. 4. Normalized number concentrations of particles as a function of time ($N(t)/N_0$) by deposition for monodisperse particles with diameters of $0.05 \mu\text{m}$ due to (a) gravitational sedimentation, (b) diffusion, (c) electrical deposition, and (d) total processes.

indicate that aerosol characteristics in a Tedlar® bag are expected to change significantly in a 1 hr period, and electrical deposition is the dominant process causing the changes.

3.2 Experimental results

Aerosol size distributions were measured at different times after introducing aerosols to characterize the stability of aerosols in a Tedlar® bag. The initial number concentration was maintained below 10^5 cm^{-3} to minimize changes in aerosol characteristics due to coagulation. Figure 2 shows the size distribution changes of aerosols in the Tedlar® bag over a 1 hr period. As can be seen in Figure 1, loss of particles in the bag is apparent, and the volume decrease with time is significant. This indicates that deposition is the main loss process for aerosols in the Tedlar® bag. The number concentration, surface area, and volume concentration of the aerosols decreased to 34%, 50%, and 52% of the initial value in 30 min, respectively (Table 3). The decreases in number concentrations were comparable to the values calculated in Table 2. These results lend credence to the hypothesis that the electrical force is the dominant loss process for par-

Table 3. Aerosol concentrations in the Tedlar® bag as a function of time.

Times (min)	Concentrations ^a		
	Number (#/cm ³)	Surface area ($\mu\text{m}^2/\text{cm}^3$)	Volume ($\mu\text{m}^3/\text{cm}^3$)
0	6.43×10^4	1370	35.9
30	2.20×10^4 (0.34)	685 (0.50)	18.6 (0.52)
60	1.75×10^4 (0.27)	543 (0.40)	15.2 (0.42)

^aValues in parentheses represent values of $N(t)/N_0$, $S(t)/S_0$, $V(t)/V_0$, determined from the experiments

ticles in a Tedlar® bag. Therefore, short duration experiments are critical to obtaining kinetic constants representative of the original aerosol conditions in a 100 L Tedlar® bag. To minimize changes in aerosol properties during the heterogeneous kinetic studies, short reaction times (less than 10 min) should be applied. Decreases in aerosol surface area were less than 10% during these time scales.

4. CONCLUSIONS

Aerosol losses in a 100 L Tedlar® bag were investigated experimentally and theoretically for the aerosols with number median diameter of $0.05 \mu\text{m}$ and number concentration of $6.4 \times 10^4 \text{ cm}^{-3}$. Over a 1 hr period, loss of particles in the bag is apparent, and the volume decrease with time is significant. The number concentration, surface area, and volume concentration of the aerosols decreased to 34%, 50%, and 52% of the initial value in 30 min, respectively. Theoretical calculations showed that coagulations and deposition by diffusion and gravitational sedimentation were not expected to change aerosol characteristics significantly, and the electrical force was the dominant loss process for particles in the Tedlar® bag over a 1 hr period. Since the aerosol losses in the bag were significant over a one hour period, short reaction times should be applied to minimize changes in aerosol properties during the heterogeneous kinetic studies. Experiments using a larger bag will help to maintain constant aerosol characteristics for longer time periods, thus allowing for enough time to perform heterogeneous kinetic

studies. The results of this study show that studies of aerosol dynamics in a reaction chamber are necessary to obtain the accurate data for heterogeneous processes.

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