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A THEORETICAL STUDY ON THE EVAPORATION OF DRY AMMONIUM CHLORIDE AND AMMONIUM NITRATE AEROSOLS

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Abstract—A theoretical model has been developed to investigate possible mechanisms and parameters which may influence the evaporation behavior of dry ammonium chloride and ammonium nitrate aerosols. The model results compared well with the experimental observations available in the literature. Effects of particle polydispersity, gas-particle interaction, flow pattern of the system, particle number concentration, and accommodation coefficient on the evaporation of dry ammonium chloride and ammonium nitrate were quantitatively determined. The particle size distribution has a significant effect on the overall evaporation rate. A negligence of the size distribution and inappropriate use of the evaporation theory would lead to departures from experimental observations.

Key word index: Ammonium chloride, ammonium nitrate, kinetic constraints, aerosol evaporation, polydispersity, annular denuder, lognormal distribution.

NOMENCLATURE

b_0	constant ($= 0.633 + 0.092\sigma_g^2 - 0.022\sigma_g^3$)	r_o	denuder outer radius
b_2	constant ($= 0.39 + 0.5\sigma_g - 0.214\sigma_g^2 + 0.029\sigma_g^3$)	r_p	particle radius
B_1	particle diffusivity ($= k_B T/(162\pi^2)^{1/3}\mu$)	S	saturation ratio
B_2	slip correction constant for diffusion ($= 3.314\lambda(\pi/6)^{1/3}$)	t	residence time
B_3	coagulation constant (continuum) ($= 2k_B T/3\mu$)	T	absolute temperature
B_4	slip correction constant for coagulation ($= 1.257\lambda(4\pi/3)^{1/3}$)	U_{av}	average gas velocity
B_5	coagulation constant (free molecule) ($= 3/4\pi)^{1/6}$ $\times (6k_B T/\rho_p)^{1/2}$	v	particle volume
B_6	evaporation constant (free molecule) ($= (36\pi)^{1/3}$)	v_g	geometric average particle volume
	$v_1 n_s (k_B T/2\pi m)^{1/2}$	v_M	molar volume of particle
B_7	evaporation constant (continuum) ($= (48\pi^2)^{1/3}/3$) $\lambda v_1 n_s (8k_B T/\pi m)^{1/2}$	v_1	molecular volume of NH_4A monomer
C_i	concentration of the gaseous species i	z	axial distance
d_p	particle diameter		
D_i	diffusion coefficient of the species i		
D_m	diffusion coefficient of monomer		
D_p	diffusion coefficient of particle		
$f(r, k)$	flow parameter term		
G	evaporation rate		
k	ratio of inner to outer radius in annular denuder		
k_B	Boltzmann constant		
K_p	equilibrium constant		
m	mass of NH_4A monomer		
M_q	q th moment of aerosol size distribution		
n	particle size distribution		
n_s	monomer concentration at saturation		
N	particle number concentration		
P_1	vapor pressure of NH_4A monomer		
P_d	vapor pressure of NH_4A monomer in equilibrium with the surface		
P_i^e	equilibrium partial pressure of species i		
r	radial position in the denuder	σ_g	geometric standard deviation
r_i	initial particle radius	ρ_p	particle density

λ mean free path of gas molecules
 μ viscosity.

INTRODUCTION

Ammonium containing aerosols (NH_4A) are commonly occurring components of atmospheric particles. The volatility of ammonium containing aerosols, especially ammonium chloride (NH_4Cl) and ammonium nitrate (NH_4NO_3), has been the interest of study of many atmospheric scientists (Richardson and Hightower, 1987; Allen *et al.*, 1989; Wexler and Seinfeld, 1991, 1992). Ammonium chloride and ammonium nitrate aerosols are formed from chemical reactions of ammonia gas with hydrochloric and nitric acids, respectively, in the atmosphere:



Allen *et al.* (1989) measured gaseous atmospheric NH_3 , HCl , and HNO_3 concentrations and compared the concentration products of $[\text{HCl}][\text{NH}_3]$ and $[\text{HNO}_3][\text{NH}_3]$ with predictions of thermodynamic equilibrium. Departures from equilibrium were remarkably observed at low temperatures ($< 5^\circ\text{C}$) and high humidities ($>$ deliquescent points of NH_4A aerosols). Pio *et al.* (1992) measured freshly emitted NH_3 , HCl and HNO_3 concentrations as well as NH_4NO_3 and NH_4Cl aerosols in industrial and marine atmospheres. They found that gas-particle equilibrium conditions are not attained instantaneously in the atmosphere. At temperatures lower than 15°C , it requires at least several minutes for the equilibrium between gaseous precursors and ammonium containing aerosols to be reached. Allen *et al.* (1989) and Pio *et al.* (1992) attributed their observations at low-temperature environment to kinetic constraints on attainment of the system equilibrium.

On the other hand, Harrison *et al.* (1990) carried out experiments on the evaporation rates of NH_4Cl and NH_4NO_3 aerosols in an annular diffusion denuder at room temperature ($\sim 20^\circ\text{C}$), and compared the results with existing transport-limited theory. The measured evaporation rates of NH_4A aerosols were significantly low as compared to the theoretical predictions. They also attributed the differences to an unknown kinetic constraints to the achievement of the system equilibrium. Based on the findings of Harrison *et al.* (1990), Harrison and MacKenzie (1990) conducted a numerical simulation and considered four kinetic mechanisms: monomer formation; adsorption of one precursor species on the particle surface; bimolecular surface reaction; and transport-limited particle growth. It was concluded that no mechanisms emerge as the rate-limiting process for all previous experimental studies. Wexler and Seinfeld (1992) incorporated a concept of characteristic time to explain the

data measured at the South Coast Air Basin of southern California. They concluded that transport limitations are a significant factor in the observed departures from equilibrium.

It seems that kinetic constraints on attainment of the $\text{NH}_4\text{A}-\text{HA}-\text{NH}_3$ system equilibrium have not been well understood and established. Theoretical studies on the evaporation of NH_4A aerosols have been restricted to chemical reaction and mass-transfer-limited particle evaporation. However, the departures of experimental observations from existing evaporation theory may also be attributed to other factors such as particle polydispersity, gas-particle interaction, flow pattern and uncertainty for the equilibrium constants of NH_4A aerosols. Therefore, a comprehensive model considering the above mechanisms is needed to quantify kinetic constraints on achievement of the gas-particle equilibrium.

This paper presents a mathematical model for simultaneous aerosol diffusion, evaporation and coagulation in terms of the moments of the aerosol size distribution over the entire particle size range. The shape of the aerosol size distribution is approximated by lognormal function. The model is then applied to simulate experimental data of dry NH_4Cl and NH_4NO_3 aerosol evaporation in an annular diffusion denuder documented by Harrison *et al.* (1990). The effects of various mechanisms on the evaporation of dry NH_4A aerosols are investigated and quantitatively determined.

THEORY

Evaporation of monodisperse particles

Since the evaporation behavior of aqueous aerosols may be fundamentally different from that of dry aerosols, the present study focuses on the evaporation process of dry NH_4Cl and NH_4NO_3 aerosols only. For a transport-limited evaporation process in the $\text{NH}_4\text{A}-\text{HA}-\text{NH}_3$ system, the aerosol evaporation rate is determined by the diffusion of a gaseous molecule through the surrounding medium. The evaporation/condensation rate for particle diameter, d_p , in the continuum regime ($\alpha d_p \gg \lambda$, where α is the accommodation coefficient and λ is the mean free path of gas molecules) is written as (Friedlander, 1977):

$$\frac{dv}{dt} = \frac{2\pi D_m d_p v_1 (p_1 - p_d)}{k_B T} \quad (3)$$

where v is the volume of a particle, t is the time coordinate, D_m and v_1 are the diffusion coefficient and molecular volume of NH_4A monomer, respectively, p_1 and p_d are the vapor pressures of NH_4A monomer in the bulk phase and in equilibrium with the surface, k_B is the Boltzmann constant, and T is the absolute temperature in Kelvin.

While for a particle whose size is in the free molecular regime ($\alpha d_p \ll \lambda$), the evaporation/condensation

rate is determined by bombardment of individual molecules as

$$\frac{dv}{dt} = \frac{\alpha \pi d_p^2 v_1 (p_1 - p_d)}{(2 \pi m k_B T)^{1/2}} \quad (4)$$

where m is the mass of NH_4A monomer.

Both Richardson and Hightower (1987) and Harrison *et al.* (1990) conducted experiments on the size change of NH_4Cl and NH_4NO_3 aerosols, and compared with the predicted results of equations (3) and (4). The evaporation rates of NH_4Cl and NH_4NO_3 aerosols obtained from their experiments were much slower than the theoretical predictions. Therefore, they have to introduce a very low accommodation coefficient in order to reconcile this divergence without a rational explanation. This indicates that equations (3) and (4) may be insufficient to predict evaporation rates of NH_4Cl and NH_4NO_3 aerosols.

Evaporation of polydisperse particles in an annular diffusion denuder

The evaporation equations (3) and (4) were simplified without considering other mechanisms such as flow pattern, aerosol size distribution, and the gas-particle interaction. A mathematical model can be derived from the general dynamic equation (GDE) that describes the change of particle size distribution function. For NH_4A particles undergoing diffusion, evaporation, and coagulation in the size range v , $v + dv$, the steady-state GDE for an aerosol stream in the annular diffusion denuder is (Friedlander, 1977)

$$U_{av} f(k, r) \frac{\partial n}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial (D_p n)}{\partial r} \right] + \frac{\partial (Gn)}{\partial v} + \frac{1}{2} \int_0^v \beta(v, v - \bar{v}) n(v) n(v - \bar{v}) d\bar{v} - \int_0^\infty \beta(v, \bar{v}) n(v) n(\bar{v}) d\bar{v} \quad (5)$$

where U_{av} is the average gas velocity through the denuder, $f(k, r)$ is the flow parameter, k is the ratio of inner to outer radius of the annular diffusion denuder, r is the radial distance inside the denuder, n is the particle size distribution function, z is the axial distance of diffusion denuder, D_p is the diffusion coefficient of particle, G is the evaporation rate, and β is the collision frequency function of Brownian coagulation. The first term on the right-hand side (RHS) accounts for particle losses by Brownian diffusion. The second RHS term accounts for the loss or gain of particles by evaporation/condensation at rate G . The third and fourth terms account for the gain and loss of particles in the interval $v, v + dv$ by Brownian coagulation. The fully developed flow parameter for an annular diffusion denuder is (Bird *et al.*, 1960)

$$f(k, r) = \frac{2[(1 - k^2) \ln(r/r_o) + \ln(1/k)(1 - r^2/r_o^2)]}{(1 + k^2) \ln 1/k - (1 - k^2)} \quad (6)$$

where r_o is the outer radius of an annular denuder.

The evaporation of NH_4A aerosols leads to the release of two gases, NH_3 and HA . The axial diffusion term can be neglected as compared to the radial diffusion term since the coated denuder wall acts as a perfect sink for the gas species. Therefore, the mass balance equation of the gaseous species i inside the annular diffusion denuder is

$$U_{av} f(k, r) \frac{\partial C_i}{\partial z} = \frac{D_i}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_i}{\partial r} \right) - \frac{1}{v_m} \int_0^\infty G n dv \quad (7)$$

where C_i is the concentration of gaseous species i ($i = \text{NH}_3$ and HA), D_i is the diffusion coefficient of species i , and v_m is the molar volume of the evaporating species. The first term on the RHS accounts for the diffusional loss of species i onto the denuder wall. The second RHS term accounts for the loss or gain of species i by evaporation/condensation at rate G .

Many experimental results indicate that aerosol size distributions are nearly lognormal or, more frequently, aerosol size distributions are measured and characterized using the parameters of a lognormal function (Pratsinis, 1988). Therefore, combining the method of moments with the lognormal distribution has the advantage of simplicity while evaluating the evolution of polydisperse aerosols. The q th moment of an aerosol size distribution is (Friedlander, 1977)

$$M_q = \int_0^\infty v^q n(v) dv \quad (8)$$

while the size distribution function, $n(v)$, for lognormally distributed aerosols is defined as

$$n(v) = \frac{N}{3\sqrt{2\pi} \ln \sigma_g} \exp \left[-\frac{\ln^2(v/v_g)}{18 \ln^2 \sigma_g} \right] \frac{1}{v} \quad (9)$$

The three parameters that completely describe a lognormal size distribution are the total number concentration, N , the geometric mean particle volume, v_g , and the geometric standard deviation based on particle radius, σ_g . The values of v_g and σ_g can be expressed in terms of the first three moments as (Lee *et al.*, 1984)

$$v_g = \frac{M_1^2}{M_0^{3/2} M_2^{1/2}} \quad (10)$$

$$\ln^2 \sigma_g = \frac{1}{9} \ln \left(\frac{M_0 M_2}{M_1^2} \right). \quad (11)$$

Thus, M_0 , M_1 and M_2 completely describe the behavior of the size distribution of a lognormally preserving aerosol. The q th moment of the distribution can be written in terms of the above parameters as

$$M_q = M_0 v_g^q \exp(4.5 q^2 \ln^2 \sigma_g). \quad (12)$$

Multiplying equation (5) by $v^q dv$ on both sides, and integrating over all particle size and using the lognormal distribution function as an approximation of the entire size spectrum, the evolution of the three aerosol

moments and the mass balance equations for the two gaseous species along the denuder are written as

$$U_{av}f(k, r) \frac{\partial M_0}{\partial z} = \frac{B_1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r} (M_{-1/3} + B_2 M_{-2/3}) \right] - \xi M_0^2 \quad (13)$$

$$U_{av}f(k, r) \frac{\partial M_1}{\partial z} = \frac{B_1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r} (M_{2/3} + B_2 M_{1/3}) \right] + \eta (S - 1) M_0 \quad (14)$$

$$U_{av}f(k, r) \frac{\partial M_2}{\partial z} = \frac{B_1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r} (M_{5/3} + B_2 M_{4/3}) \right] + 2\xi M_1^2 + 2\varepsilon (S - 1) M_1 \quad (15)$$

$$U_{av}f(k, r) \frac{\partial C_{NH_3}}{\partial z} = \frac{D_{NH_3}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{NH_3}}{\partial r} \right) - \frac{\eta}{v_M} M_0 (S - 1) \quad (16)$$

$$U_{av}f(k, r) \frac{\partial C_{HA}}{\partial z} = \frac{D_{HA}}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_{NH_3}}{\partial r} \right) - \frac{\eta}{v_M} M_0 (S - 1) \quad (17)$$

where M_0 , M_1 and M_2 represent the total particle number concentration, total particle volume, and second volume moment, respectively, B_1 and B_2 are the particle diffusivity constant and the slip correlation constant for diffusion, ξ and ζ denote the coagulation coefficients for zero and second moments, η and ε are the evaporation/condensation coefficients for the first and second moments, and S is the system saturation ratio. The parameters of ξ , ζ , η and ε were derived for particles in the free molecular and continuum regimes, respectively. A harmonic average of the two regimes is then employed for the entire particle size range. The detailed derivations of B_1 , B_2 , ξ , ζ , η and ε can be seen in Kim and Pratsinis (1988) and Pratsinis (1988), and their definitions are listed in the Nomenclature.

The initial conditions for equations (13)–(17) are obtained from the experimental inlet conditions of Harrison *et al.* (1990). Assuming that the NH_4A aerosol streams generated from an atomizer are free of gases at the inlet of the denuder, the initial conditions are

$$\text{at } z=0, \quad M_0 = N_i, \quad M_1 = N_i v_{gi} \exp(4.5 \ln^2 \sigma_{gi}), \quad M_2 = N_i v_{gi}^2 \exp(18 \ln^2 \sigma_{gi}), \quad (18)$$

$$C_{HA} = C_{NH_3} = 0$$

where subscript i represents the inlet condition of the annular denuder system.

The boundary conditions for particles with the assumption of no resuspension once they arrive at both inner and outer denuder walls are

$$\text{at } r = kr_o \text{ and } r = r_o, \quad M_0 = M_1 = M_2 = 0 \quad (19)$$

while the boundary conditions for gaseous species i are $C_i = 0$ for a perfect sink wall coated with absorbing material and $\partial C_i / \partial r = 0$ for an inert wall.

Equations (13)–(17) along with the appropriate initial and boundary conditions form a set of coupled partial differential equations (PDE) that describes the

behavior of dry NH_4A aerosols and associated gases in an annular diffusion denuder. Using an explicit finite-difference scheme at P radial points across the denuder, the five PDEs are transformed to $5 \times P$ ordinary differential equations (ODE). These ODEs are then solved by a stiff ordinary differential equation solver, DIVPAG (IMSL, 1987). The cup mixing average (X_{av}) of the moments and gaseous concentrations inside the denuder at any location z is calculated by

$$X_{av}(z) = \frac{\int_{kr_o}^{r_o} X(r, z) U_{av}f(r) r dr}{\int_{kr_o}^{r_o} U_{av}f(r) r dr} \quad (20)$$

where $X = M_0$, M_1 , M_2 , C_{NH_3} , C_{HCl} , and C_{HNO_3} .

RESULTS AND DISCUSSION

Model verification

The present model was first investigated under limiting conditions where analytical solutions were available for pure particle diffusion, pure particle evaporation/condensation, pure particle coagulation and pure gas diffusion. The numerical solutions for pure gas diffusion and pure particle diffusion were in excellent agreement with the Gormley–Kennedy solution (Gormley and Kennedy, 1949). The evaporation rates of monodisperse aerosols in the continuum and free molecular regimes were validated by equations (3) and (4), respectively. The pure particle coagulation for a monodisperse aerosol was also verified by comparing the simulated number concentration with Hinds (1982, figure 12.1). The model results for polydisperse aerosols were confirmed with the geometric standard deviation, σ_g , asymptotically approaching 1.35 and 1.32 for pure particle coagulation in the free molecular and continuum regimes, respectively (Lee *et al.*, 1984), and unity when only condensation was considered (Pratsinis, 1988). In addition, possible numerical artifacts were further minimized by letting σ_g close to 1, and compared the model prediction to those obtained analytically with a monodisperse distribution.

The model is then applied to simulate the experimental data of dry NH_4Cl and NH_4NO_3 aerosol evaporation in an annular diffusion denuder documented by Harrison *et al.* (1990). Their experimental conditions are summarized as: the denuder was 100 cm long with an inner diameter of 3.7 cm and outside diameter of 4 cm which provided a value of k equal to 0.925. The inner tube was coated with 5% methanolic solution of citric acid or phosphorous acid for collecting NH_3 , whilst the outside tube was coated with 5% $NaOH$ in methanol for HCl collection and a suspension of MgO powder in methanol for HNO_3 collection. The coating length was 88 cm, the first 12 cm of the denuder was left uncoated to establish a laminar fully developed air flow. Since the flow rate through the denuder was less than 100 ml min^{-1} , the Reynolds number is well within the laminar flow regime. The experimental system was operated at

$20 \pm 2^\circ\text{C}$. Ammonium chloride and ammonium nitrate aerosol streams were generated by a TSI atomizer (Model 9302). The initial geometric mean radius and geometric standard deviation were $0.53 \mu\text{m}$ and 1.67 for NH_4Cl aerosols, and $0.46 \mu\text{m}$ and 1.6 for NH_4NO_3 aerosols, respectively.

The initial number concentrations of NH_4Cl and NH_4NO_3 particles in the aerosol streams were not reported in the study of Harrison *et al.* (1990). However, according to Agarwal and Johnson (1981), the typical range of particle number concentration generated from an atomizer of TSI Model 9302 should lie between 10^4 and 10^7 cm^{-3} . Therefore, initial particle number concentration was selected as 10^5 cm^{-3} in the simulation. The accommodation coefficient α was set to unity (Raes *et al.*, 1990). These two parameters are uncertain in the numerical simulation and will be examined in the sensitivity analysis. The diffusivities of NH_3 , HNO_3 and HCl used in the model were equal to 0.227, 0.118 (Winiwarter, 1989) and $0.1167 \text{ cm}^2 \text{ s}^{-1}$ (Reid *et al.*, 1988), respectively.

The equilibrium constant of NH_4Cl particles with the two associated gases, NH_3 and HCl , was taken from Pio and Harrison (1987):

$$\begin{aligned} \ln(K_p) = & 2.2358 \ln T - \frac{2.13204 \times 10^4}{T} + 65.4375 \\ & - 8.167 \times 10^{-3} T + 4.644 \times 10^{-7} T^2 \\ & - 1.105 \times 10^{-10} T^3 \end{aligned} \quad (21)$$

while the equilibrium constant of NH_4NO_3 particles with the two associated gases, NH_3 and HNO_3 , were taken from Stelson and Seinfeld (1982):

$$\ln(K_p) = 84.6 - \frac{24,220}{T} - 6.1 \ln\left(\frac{T}{298}\right) \quad (22)$$

or from Mozurkewich (1993):

$$\ln(K_p) = 118.87 - \frac{24,084}{T} - 6.025 \ln T. \quad (23)$$

The NH_4A monomer concentration in the bulk phase can be written as $p_1 = S \times p_d$, where p_d is commonly expressed as $p_d = p_{\text{NH}_3}^e + p_{\text{HA}}^e = 2K_p^{1/2}$ (Harrison and MacKenzie, 1990), and superscript e denotes the state of equilibrium. The system saturation ratio S is defined as (Kodas *et al.*, 1986)

$$S = \frac{C_{\text{NH}_3} C_{\text{HA}}}{K_p}. \quad (24)$$

When the value of saturation ratio is unity, the system is in an external state of equilibrium. The driving force of the evaporation process of NH_4A aerosols is determined by $(1 - S)$.

Figures 1 and 2 show measured and simulated results on the change of particle radius of dry NH_4Cl and NH_4NO_3 aerosols in the annular diffusion denuder, respectively. It is seen that the simulated results agree well with the experimental data.

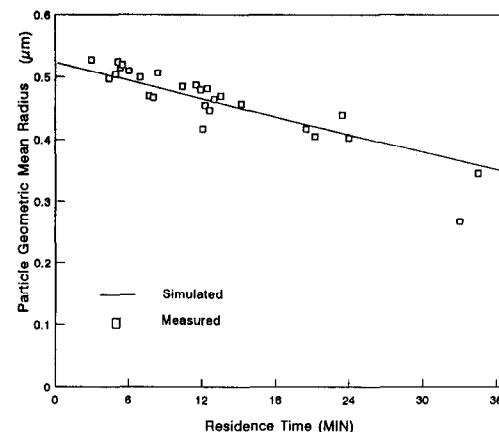


Fig. 1. Measured and simulated results on the change of particle radius of dry ammonium chloride aerosols in an annular denuder.

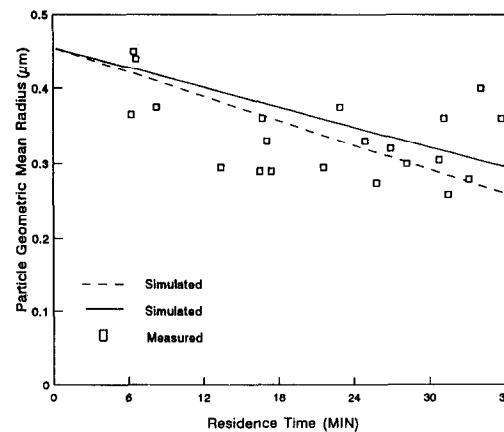


Fig. 2. Measured and simulated results on the change of particle radius of dry ammonium nitrate aerosols in an annular denuder. (Dashed line) $K_p = 11.58 \text{ ppb}^2$ (Mozurkewich, 1993), (solid line) $K_p = 7.7 \text{ ppb}^2$ (Stelson and Seinfeld, 1982).

Table 1 lists regression equations of the rate of particle radius change (dr_p/dt) for the experimental data of Harrison *et al.* (1990) as well as for numerical data of the present model. The regression equations of the experimental data were obtained directly from Harrison *et al.* (1990). The rate equations from the present model were obtained by a linear regression of 200 points of numerical data. The correlation coefficients were 0.9999 for both NH_4Cl and NH_4NO_3 aerosol evaporation in the annular diffusion denuder. This indicates that dr_p/dt obtained from the model simulation is approximately constant with respect to the residence time in the case of study. As shown in Table 1, the values of dr_p/dt calculated from the present model for NH_4NO_3 particle evaporation are higher than that obtained by Harrison *et al.* (1990), whether values of K_p were obtained from either Stelson and Seinfeld (1982) or Mozurkewich (1993). However, the regression result of Harrison *et al.* (1990)

Table 1. Regression equations of particle radius change for the experimental data of Harrison *et al.* (1990) and numerical results of the present model*

	NH_4NO_3	NH_4Cl
Experimental results	$r_p = 0.40 - 0.0027 t$	$r_p = 0.54 - 0.0063 t$
Model results	$\dagger r_p = 0.45 - 0.0044 t$	$r_p = 0.52 - 0.0048 t$
	$\ddagger r_p = 0.45 - 0.0054 t$	

* The units in $r_p = r_i - (dr_p/dt)t$ are minute for t and μm for r_p and r_i . The regression equations of our numerical data are not valid for residence times longer than experimental residence times of Harrison *et al.* (1990).

† Simulation of the equilibrium constant obtained from Stelson and Seinfeld (1982).

‡ Simulation of the equilibrium constant obtained from Mozurkewich (1993).

indicated an initial particle radius of $0.40 \mu\text{m}$, which is higher than that of their experimentally measured value, $0.46 \mu\text{m}$. Therefore, if the regression were made by an initial radius of $0.46 \mu\text{m}$ instead of $0.4 \mu\text{m}$, better agreement of dr_p/dt would be obtained. A similar comparison for the regression equations of NH_4Cl particle evaporation can also be made from Table 1 between experimental data and model simulation.

Limiting mechanisms for the NH_4A evaporation process

Harrison and MacKenzie (1990) indicated that the departure of experimental data of Harrison *et al.* (1990) from the evaporation theory (equations (3) and (4)) requires at least a 49-fold inaccuracy in one of the parameters, D_m , v_m and p_d . The diffusivities of NH_4Cl and NH_4NO_3 vapors were estimated as (Pratsinis, 1988)

$$D_m = \frac{\lambda(8k_B T/\pi m)^{1/2}}{3}. \quad (25)$$

The corresponding values of D_m for NH_4Cl and NH_4NO_3 vapors are 7.38×10^{-2} and $6.03 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$, respectively. These data were one-third of those used in Harrison *et al.* (1990). Values of v_m and p_d of NH_4Cl monomers used in the model were in accord with those of Harrison and MacKenzie (1990) and Harrison *et al.* (1990). Different values of p_d for NH_4NO_3 monomers were obtained from equilibrium constants documented by Stelson and Seinfeld (1982) and Mozurkewich (1993), and their effects are shown in Fig. 2. Values of these two p_d were also about the same order of magnitude as that of Harrison *et al.* (1990). Therefore, it appears that there are other mechanisms or factors than the three parameters which influence the evaporation process of dry NH_4Cl and NH_4NO_3 aerosols.

An investigation of other mechanisms incorporated in the present model is illustrated in Figs 3 and 4 for NH_4Cl and NH_4NO_3 particle evaporation, respectively. Several hypotheses were considered and indicated in number in Figs 3 and 4 as follows.

(i) Evaporation of monodisperse aerosols by diffusion process in the continuum regime (equation (3)) was incorporated with $p_1 = 0$.

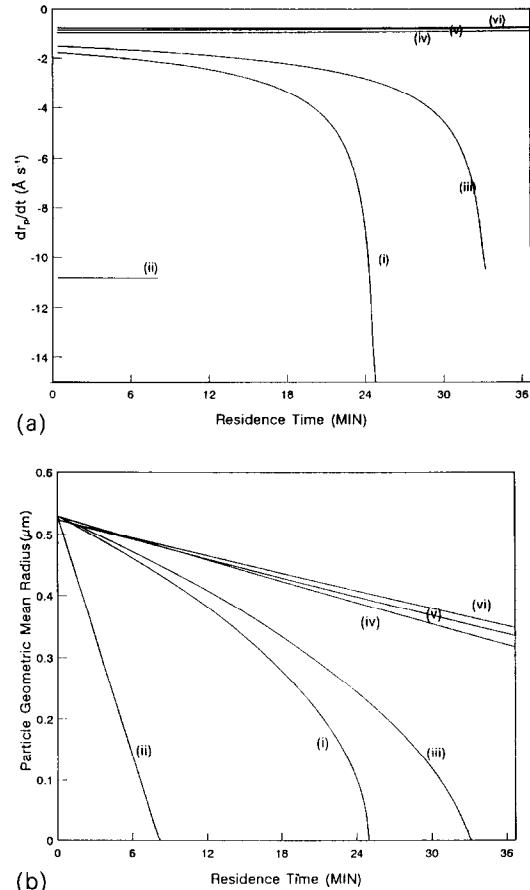


Fig. 3. Simulated results of hypotheses (i)–(vi) for ammonium chloride aerosols in an annular denuder: (a) the rate of change of particle radius; (b) the change of particle radius.

(ii) Evaporation of monodisperse aerosols by molecular bombardment in the free molecular regime (equation (4)) was incorporated with $p_1 = 0$.
 (iii) A harmonic average of hypothesis (i) and (ii) was incorporated over the entire particle size range (Pratsinis, 1988).
 (iv) In addition to hypothesis (iii), the GDEs (equations (13)–(15)) with a lognormally distributed function were incorporated with initial geometric

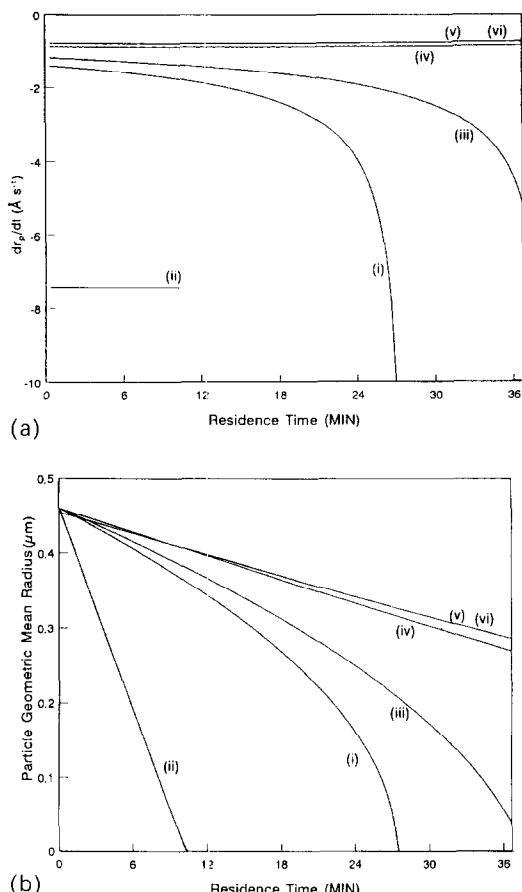


Fig. 4. Simulated results of hypotheses (i)–(vi) for ammonium nitrate aerosols in an annular denuder: (a) the rate of change of particle radius; (b) the change of particle radius.

standard deviations of 1.67 and 1.6 for NH_4Cl and NH_4NO_3 aerosols, respectively, and a uniform velocity profile ($f(k, r) = 1$).

(v) In addition to hypothesis (iv), a fully developed flow pattern (equation (6)) in an annular diffusion denuder was incorporated.

(vi) In addition to hypothesis (v), values of p_1 were not zero. Instead, they were obtained from the mass balance equations of gaseous species (equations (16) and (17)).

Note that the simulation results shown previously in Figs 1 and 2 were obtained from hypothesis (vi) which was considered as a complete model. Figures 3a and 4a show the rate of change of particle radius (dr_p/dt) and Figs 3b and 4b show the change of particle radius, r_p , with respect to residence time for NH_4Cl and NH_4NO_3 aerosols in an annular denuder, respectively. As can be seen, values of $-dr_p/dt$ are maximum and constant when hypothesis (ii) was considered at a small residence time. Therefore, both NH_4Cl and NH_4NO_3 particles evaporated completely in a short time (~ 10 min). On the other hand, when hypothesis (i) was considered, values of $-dr_p/dt$

were small at the beginning, and then increased rapidly as particles continued the evaporation process. As particles become very small, values of $-dr_p/dt$ approached infinity where hypothesis (i) was actually not valid. The time required for complete evaporation of NH_4Cl and NH_4NO_3 particles with initial radii of 0.53 and 0.46 μm are 24.9 and 27.4 min, respectively, for hypothesis (i) to be applied. These values are longer than those estimated by Harrison and MacKenzie (1990) and Harrison *et al.* (1990) (8.7 and 5.3 min for NH_4Cl and NH_4NO_3 aerosols, respectively) using the same theory. The difference was attributed to different values of D_m employed.

Since the initial radii of NH_4Cl and NH_4NO_3 particles in the experiment of Harrison *et al.* (1990) fall in the transition regime ($0.1 < \lambda/r_p < 10$), hypothesis (iii) should be more appropriate to explain the experimental data. It was clearly indicated in Figs 3a and 4a that values of $-dr_p/dt$ predicted from hypothesis (iii) are smaller than those predicted from hypotheses (i) and (ii). It is also seen that as the residence time was short (which represents larger particles as shown in Figs 3b and 4b), values of dr_p/dt obtained from hypothesis (iii) approached to that obtained from hypothesis (i). As the residence time was long (small particles), values of dr_p/dt obtained from hypothesis (iii) approached to that obtained from hypothesis (ii). They were identical at the instant that particles evaporated completely.

Another important result obtained from Figs 3 and 4 is that particle polydispersity plays a very important role on the overall evaporation rate. This was demonstrated from hypothesis (iv) where aerosols with a log-normal size distribution were assumed. The particle evaporation rates were remarkably retarded as compared to hypothesis (iii). Values of dr_p/dt obtained from hypothesis (iv) were approximately constant with respect to residence time.

On the other hand, results from hypotheses (v) and (vi) did not show significant departures from hypothesis (iv). This indicates that the effects of flow pattern ($f(k, r)$) and vapor pressure in the bulk phase, p_1 , on the rate of change of particle radius are negligible in the case of study.

In the present study it was assumed that dry NH_4Cl and NH_4NO_3 aerosols were in an internal state of equilibria and values of p_d could be estimated from the thermodynamic equilibrium constants. Therefore, although the assumption of zero inlet gas concentrations was made in the numerical simulation, the NH_4Cl and NH_4NO_3 aerosols evaporate and release gases immediately after entering the denuder in order to approach their internal equilibrium values. As a result, there will be minimum effect whether the inlet gas concentrations were zero or at their maximum equilibrium concentrations. However, departures from the external equilibria occur due to diffusional absorption of gas species to the denuder wall. The departures from external equilibrium were estimated by the saturation ratio as shown in Fig. 5 for evaporation of

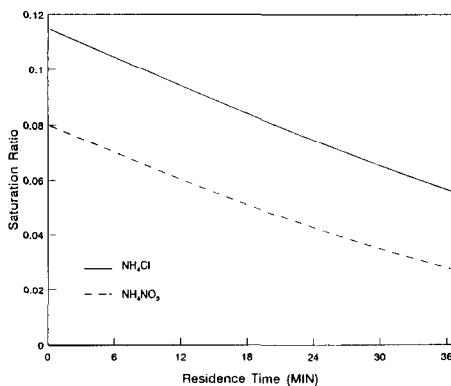


Fig. 5. Variations of saturation ratio with respect to residence time for ammonium chloride and ammonium nitrate aerosols in an annular denuder.

NH_4Cl and NH_4NO_3 aerosols in the annular denuder. The saturation ratio was maximum upon entering the denuder, but decreased rapidly due to diffusional adsorption to the denuder wall. Since diffusion denuder acts as a perfect sink for the adsorbing gases, the deposition rates of gaseous species are infinitely large and therefore the system saturation ratios are quite low. The decrease of the saturation ratio as an increase of the residence time also indicated that the diffusion rate of gaseous species to the denuder wall is faster than the evaporation rate.

Sensitivity analysis

As indicated previously, the NH_4Cl and NH_4NO_3 particle number concentrations were not reported by Harrison *et al.* (1990). Since the particle number concentration influences both the rates of evaporation and coagulation, it would also influence the change of NH_4A particle radius. Figure 6 shows a sensitivity analysis of varying particle number concentration on the change of particle radius of dry NH_4Cl aerosols in the denuder. As can be seen, for particles whose number concentrations were in the range of 10^4 – 10^5 cm^{-3} , the effect of number concentration on the particle evaporation was negligible. However, as the particle number concentration was increased, the particle radius change slowed down due to a retardation of particle evaporation rate and an increase of particle coagulation rate. If the particle number concentration was higher than 10^6 cm^{-3} , the NH_4Cl particle radius was increased with an increase of residence time. This is obviously not the case of the experimental observation of Harrison *et al.* (1990). Similar results can be drawn for NH_4NO_3 aerosol evaporation. Therefore, it may be concluded that particle number concentration in the experiments of Harrison *et al.* (1990) was in a relatively low range (10^4 – 10^5 cm^{-3}) where Brownian coagulation effect is negligible.

The other uncertainty in the numerical simulation is that the accommodation coefficient may not be unity. A sensitivity analysis was performed in order to

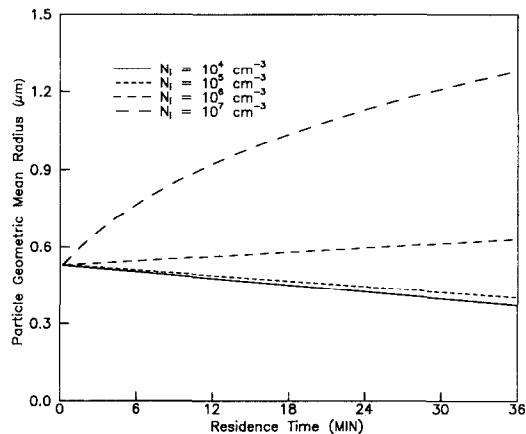


Fig. 6. Effects of varying particle number concentration on the change of particle radius of ammonium chloride aerosols in an annular denuder. The accommodation coefficient was unity in all simulations.

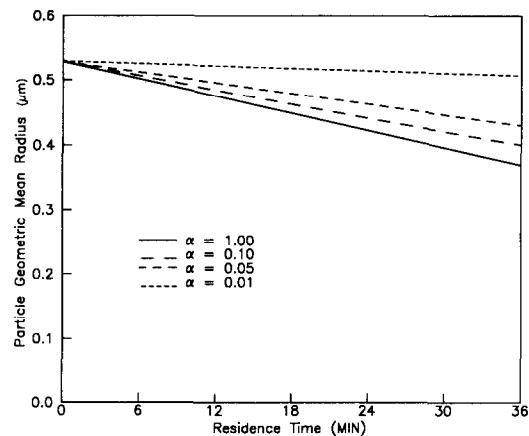


Fig. 7. Effects of varying accommodation coefficient on the change of particle radius of ammonium chloride aerosols in an annular denuder. The particle number concentration was 10^4 cm^{-3} in all simulations.

explore the effect of varying accommodation coefficient on the change of particle radius of dry NH_4Cl aerosols in the denuder. This was done using the lowest possible number concentration of 10^4 cm^{-3} in the simulation. This number concentration was selected as it resulted in the fastest evaporation rate as shown in Fig. 6, and the evaporation rate could be retarded by lowering the accommodation coefficient. Results of a sensitivity analysis of varying accommodation coefficient are shown in Fig. 7. As can be seen, if the experiments of Harrison *et al.* (1990) were done under particle number concentration of 10^4 cm^{-3} , then the accommodation coefficient may be in the range 0.1–1. This is about an order of magnitude larger than that estimated by Wexler and Seinfeld (1990), who assumed a range of 0.02–0.1 in

their calculations. This may be attributed to a negligence of particle polydispersity in their study. On the other hand, if the experimental particle number concentration was around 10^5 cm^{-3} , the accommodation coefficient should be close to unity.

CONCLUSIONS

In this study a mathematical model has been developed to investigate possible mechanisms and parameters that lead to discrepancies of the experimental observations from existing theories of aerosol evaporation in the literature. The performance of the model was validated by comparing its predictions with known solutions at certain limiting cases and then was successfully applied to simulate the experimental data of Harrison *et al.* (1990) in an annular diffusion denuder at a temperature of around 20°C. The transport-limited particle evaporation theory should be a valid assumption for the case of dry NH_4Cl and NH_4NO_3 aerosols. However, it requires a modification for particles whose sizes fall in the transition regime. In addition, a negligence of particle polydispersity in the theoretical investigation would also lead to a significant deviation from the experimental observation. Therefore, only if the effect of size distribution is considered, a quantification of kinetic constraints on the evaporation behavior would become possible.

The present study demonstrated that the approach of evaporation process to gas-solid particle equilibrium is transport-limited at higher ambient temperatures. Wexler and Seinfeld (1992) also hypothesized a transport-limited particle evaporation process in their study. However, it is believed by the authors of the present study that chemical reaction limitation is also possible under cold weather conditions due to the fact that chemical reaction rate decreases as temperature decreases. This may explain the observations of Allen *et al.* (1989) that disequilibrium effects were significant at temperatures below 5°C, while the measured data were in a better agreement with the thermodynamic predictions at temperatures above 5°C. Unfortunately, limited data are available on the chemical kinetics of $\text{NH}_4\text{A}-\text{NH}_3-\text{HA}$ system. Therefore, a quantification of whether the approach to gas-solid particle equilibrium at low temperature conditions is transport-limited or chemical-reaction-limited is not possible at the present time.

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