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A model of aerosol evaporation kinetics in a thermodenuder

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Abstract

Aerosol thermodenuders provide a measure of particle volatility. The information provided by a thermodenuder is fundamentally related to the kinetics of evaporation and condensation within the device. Here, a time-dependent, multi-component model of particle and gas-phase mass transfer in a thermodenuder is described. This model explicitly accounts for the temperature profile along the length of a typical thermodenuder and distinguishes between the influence of the heating section and of the adsorbent denuder section. It is shown that “semi-volatile” aerosol is particularly sensitive to the inclusion of the adsorbent denuder in the model. As expected, the mass loss from particles through the thermodenuder is directly related to the compound vapor pressure, although the assumptions regarding the enthalpy of vaporization are shown to also have a large influence on the overall calculated mass thermograms. The model has been validated by comparison with previously measured mass thermograms for single-component aerosols and is shown to provide reasonable semi-quantitative agreement. The model that has been developed here can be used to provide quantitative understanding of aerosol volatility measurements of single and multi-component aerosol made using thermodenuders.

1 Introduction

In recent years aerosol thermodenuders have become an important tool used to assess aerosol volatility in both the lab and field (Burtscher et al., 2001; Wehner et al., 2002, 2004; Kalberer et al., 2004; An et al., 2007; Denkenberger et al., 2007; Huffman et al., 2008, 2009a,b; Asa-Awuku et al., 2009; Faulhaber et al., 2009; Grieshop et al., 2009; Kostenidou et al., 2009; Kroll et al., 2009). In a typical aerosol thermodenuder (or TD), particles in a flowing air stream are heated to a fixed temperature for a specific period of time. This increase in temperature provides a driving force which induces evaporation of compounds from particles. Following the heating section, the particles

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are cooled and passed through an activated carbon denuder which is designed to (1) remove gas-phase organic species and (2) minimize re-condensation on the particles. Once the particles leave the thermodenuder can be directed to any number of different instruments where chemical, size or physical property measurements can be made.

With few exceptions (Faulhaber et al., 2009) studies to date have used aerosol thermodenuder measurements to provide only a qualitative description of aerosol volatility. It has been established that an assumption that thermodynamic equilibrium at the temperature of the denuder is reached may lead to misinterpretation of observations (An et al., 2007) given that the behavior of particles in a thermodenuder is fundamentally determined by the kinetics of the evaporation process. As such, quantitative understanding and interpretation of the effect of heating on particle composition necessarily requires the use of a detailed microphysical evaporation model. As particles are heated in a thermodenuder, the individual compounds comprising the particles evaporate at a rate determined by the thermodynamic properties of each individual compound (vapor pressure at ambient temperature and enthalpy of vaporization), the mole fraction of that compound in the particles (accounting for Raoult's Law) and the strength of non-ideal interactions with the other particle components. Note that implicit in this discussion is the assumption that the particles exhibit liquid-like behavior (Marcolli et al., 2004; Cappa et al., 2008), and are therefore well-mixed on the time scale of the evaporation process. In addition, mass transfer limitations, re-condensation upon cooling and loss of gas-phase species and particles in the denuder must be accounted for.

Here, the development of a detailed kinetic model of evaporation, which can be used to quantitatively interpret measurements of organic aerosol volatility made using thermodenuders, is reported on. One particular aspect of our model which distinguishes it from others (e.g. Faulhaber et al., 2009) is that the influence of the adsorbent *denuder* section of the thermodenuder has been explicitly included and also the velocity gradient across the thermodenuder tube has been accounted for.

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2 Kinetic model of aerosol evaporation

A two-stage model of a thermodenuder (heated tube+denuder) has been developed for use in the analysis of TD experiments. This model can be used to explore the influence of the choice of evaporation coefficient, the volatility (vapor pressure) distribution and the enthalpy of vaporization distribution on evaporation in a thermodenuder. Details of this model are described below.

The TD model developed here is an extension of the annular diffusion denuder model of (Pratsinis et al., 1989) to a cylindrical tube geometry (Gormley and Kennedy, 1949) with temperature-dependent evaporation of a multi-component aerosol (Cappa et al., 2008). The mass balance equation for the gas-phase molecules along the x -axis can be written as

$$u(r) \frac{\partial C_{g,i}(r)}{\partial x} = \frac{D_i}{r} \frac{\partial}{\partial r} \left[r \frac{\partial C_{g,i}}{\partial r} \right] - 2\pi N_p D_i d_p(r) [C_{g,i}(r) - C_{\text{sat},i}(T) \chi_i(r)] \Gamma(r, T), \quad (1)$$

where $u(r)$ is the linear velocity, $C_{g,i}(r)$ is the gas-phase concentration (molecules/m³) of species i , D_i is the gas-phase diffusion coefficient, $d_p(r)$ is the particle diameter, $C_{\text{sat},i}$ is the temperature-dependent saturation concentration of species i , N_p is the particle number concentration, $\chi_i(r)$ is the particle phase mole fraction of species i (needed to account for Raoult's Law), r is the radial distance and x is the direction of flow. The first term on the right hand side describes diffusion of the gas-phase along the tube radius and the second term describes the gain/loss in gas phase molecules due to evaporation/condensation of the particles. The linear velocity is assumed to vary as

$$u(r) = \frac{2Q(T)}{\pi a^4} [a^2 - r^2], \quad (2)$$

where $Q(T)$ is the temperature-dependent volumetric flowrate and a is the tube radius. The volumetric flowrate increases with temperature, but the shape of the velocity profile

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is assumed to be unaffected by the heating or cooling. $\Gamma(r, T)$ is a term which accounts for non-continuum effects in the mass transfer process and is given by

$$\Gamma(T, r) = \frac{0.75\gamma_e(1 + Kn)}{Kn^2 + Kn + 0.283Kn\gamma_e + 0.75\gamma_e}, \quad (3)$$

where γ_e is the evaporation coefficient (or mass accommodation coefficient) and Kn is the Knudsen number (Seinfeld and Pandis, 1998). The Knudsen number is defined as $2\lambda/d_p$, where λ is the mean-free-path of the evaporating molecule in air. The radial dependence of Γ comes from the radial dependence of d_p . λ is estimated as $3D_i/v_{rms}$ where v_{rms} is the root mean square speed of the evaporating molecule, which is given by $\sqrt{8RT/\pi MW_i}$ with R being the ideal gas constant and MW_i the molecular weight. The evaporation coefficient is defined as the ratio between the actual evaporation rate divided by the theoretical maximum evaporation rate, as given by the Hertz-Knudsen equation (Kulmala and Wagner, 2001). Unless otherwise specified, it has been assumed here that $\gamma_e=1$ (although this value can be adjusted as desired).

For particles, the equivalent mass-balance equation is

$$u(r) \frac{\partial C_{p,i}(r)}{\partial x} = 2\pi D_i d_p(r) [C_{g,i}(r) - C_{sat,i}(T) \chi_i(r)] \Gamma(r, T), \quad (4)$$

where $C_{p,i}$ is the particle phase concentration of species i (in molecules/particle).

The saturation concentrations for use in Eq. (1) are calculated from their values at $T_{ref}=298$ K according to

$$C_{sat}(T_d) = C_{sat}(T_{ref}) \left[\frac{T_{ref}}{T_d} \right] \exp \left(\frac{-\Delta H_{vap}}{R} \left[\frac{1}{T_d} - \frac{1}{T_{ref}} \right] \right), \quad (5)$$

where ΔH_{vap} is the (compound-specific) enthalpy of vaporization and T_d is the heated section temperature. The C_{sat} values are calculated explicitly at every time step of

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the model and depend on the specific temperature profile that is used. The saturation concentrations are related to vapor pressures through the equation

$$C_{\text{sat}} = \frac{\zeta 10^6 MW p_{\text{sat},l}}{RT}, \quad (6)$$

where $p_{\text{sat},l}$ is the sub-cooled liquid vapor pressure and ζ is the activity coefficient (here assumed to be unity).

The initial distributions between gas and particle phase are calculated assuming equilibrium conditions, as discussed further below. Starting from the initial ambient temperature gas/particle distribution, Eqs. (1) and (4) are numerically integrated forward in time (i.e. distance). To facilitate numerical integration, the system is divided into a series of concentric cylinders each with their own d_p , χ_i , $C_{g,i}$, etc. The average particle residence time in the hot section (t_{res}) is determined based on the area-weighted average velocity and specified heated tube and denuder lengths (L_{hot} and L_{denuder}). Note that because the volumetric flowrate is temperature dependent, the velocity and residence time through the heated section are temperature dependent, with $t_{\text{res}}(T_d) = t_{\text{res}}(T_{\text{ref}})[T_{\text{ref}}/T_d]$. New χ_i values are determined for use in the next time step based on the updated $C_{p,i}$. Similarly, the particle diameter is recalculated at each time step. Although each compound is allowed to have a unique molecular weight, the simplifying assumption that the densities of all species are the same has been made (this assumption can be relaxed as desired).

In the TD model, particles and gases, initially in equilibrium at 298 K (see below), are first heated to the temperature of the heated section (specified as T_d). In the heated section, it is assumed that there is no loss of gas-phase molecules to the walls, although there is mass transport of gas-phase molecules between bins due to the formation of a radial concentration gradient. At the end of the heated section the system is returned to ambient temperature; for both the heating and cooling zones in the heated section, the temperature changes were specified to take place over a distance equal to 15% of the total heated section length (Fig. 1). This distance was chosen so as to be

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generally consistent with the measured temperature profile in a recent thermodenuder design (Huffman et al., 2008). In the denuder section, the walls were assumed to be a perfect sink for gas-phase molecules, which amounts to setting a boundary condition that $C_{g,i}(a)=0$. Loss of gas-phase molecules to the walls of the denuder leads to depletion of the gas phase near the walls and the establishment of a concentration gradient across the tube. This perturbation will disturb any equilibrium that might have been established in the heated region and will lead to further evaporation of all compounds from the particles. However, in the absence of wall losses the decrease in temperature will lead to a condition where $C_{g,i} > \chi_i C_{\text{sat},i}$ and therefore cause re-condensation onto the particles; in going from the heated section to the denuder section there are competing forces at work. It is worth reiterating that, unlike the denuder section, it has been assumed that the walls of the heated section do not adsorb gas-phase molecules, i.e. the evaporated molecules remain in the gas-phase. It is possible that the walls of the heated section may act, to some extent, as a sink for gas-phase molecules. However, the efficiency with which any adsorption process might occur in this section will undoubtedly decrease rapidly as the temperature in this section increases (Atkins and De Paula, 2006), making it difficult to account for quantitatively. Furthermore, it is likely that adsorption by the walls in the heated section would be significantly less efficient than by the charcoal in the denuder section given (1) the larger surface of the charcoal and (2) the likely stronger binding between the adsorbed molecules and the charcoal than the adsorbed molecules and the (stainless steel) tube walls. The assumption of no gas-phase losses in the heated section provides for a lower limit on the extent of particle evaporation in the heated section as particle evaporation in this case will cease once the gas-phase becomes saturated.

For all calculations here $L_{\text{hot}}=58$ cm long with $D_{\text{hot}}=2.2$ cm and $L_{\text{denude}}=41$ cm long with $D_{\text{denude}}=1.9$ cm (Huffman et al., 2008); as with all of the design-specific parameters used here, these can be easily adjusted to model any given thermodenuder design. Note that the residence times reported here have been calculated based on the time spent in the fully heated region ($L=41$ cm), not including the heating and cooling zones.

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In some instances (depending on the specified vapor pressure, flow rate, temperature, etc.) the particles completely evaporate in the heated section. It has been assumed that nucleation does not occur in the system. Although nucleation may occur in real thermodenuders, it is reasonable to exclude it here because these nucleated particles will typically be easily identifiable as a mode separate from the particles of interest. The nucleated particles can therefore easily be excluded in the final analysis of real measurements.

To produce mass thermograms, the time/distance-dependent model is run once for each T_d value and from this the variation in the particle diameter, total particle mass and compound specific particle mass are determined as a function of thermodenuder temperature. Typically, the resultant particle mass values are normalized to the values at some reference temperature and thus the mass fraction remaining (MFR) can be determined as a function of temperature for comparison with experiment. Calculation of the MFR requires that a reference state be defined. Here, two choices of this reference state are considered: (1) where the aerosol has bypassed the thermodenuder and (2) where the aerosol has passed through the thermodenuder at T_{ref} , which is equivalent to the aerosol passing only through the denuder section. These will be referred to as MFR_{bp} and MFR_d , respectively. As an additional case, the MFR has been calculated for aerosol passing only through the heated section. In this case, use of either reference condition yields equivalent MFR values, referred to as MFR_h . Note that MFR_{bp} is the parameter most directly comparable to previously reported measurements (e.g. Huffman et al., 2008).

The system (particles+gas-phase) are assumed to be in equilibrium when they enter the thermodenuder. The equilibrium composition of both particles and the gas-phase for a given amount of total organic mass comprised of i different compounds is calculated according to absorptive partitioning theory (Pankow, 1994), where the compound specific particle mole fraction is given by (Donahue et al., 2006)

$$\xi_i = (1 + MW_{OA}C_{sat,i}/MW_iC_{OA})^{-1}, \quad (7)$$

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where C_{OA} is the total organic mass loading ($\mu\text{g}/\text{m}^3$), $C_{\text{sat},i}$ is the effective saturation concentration of compound i ($\mu\text{g}/\text{m}^3$), MW_i is the molecular weight of compound i and MW_{OA} is the average molecular weight of the compounds comprising the aerosol. Here, the equation given by Donahue et al. has been modified to explicitly include molecular weight.

3 Results and discussion

The thermodenuder model described above includes separate heated and denuder sections. A previously published model of particle evaporation in a thermodenuder considered only the heated section (Faulhaber et al., 2009). Additionally, this previous model did not account for the variable residence times experienced by particles in the heated section due to the velocity profile across the tube diameter. Differences between our model and the Faulhaber model, in particular to the effects of the inclusion of the denuder section and velocity profile, are explored here.

3.1 Influence of gas velocity

The calculated MFR is found to change slightly more steeply with temperature when a constant velocity is assumed compared to when the velocity profile given as Eq. (2) is used (Fig. 2). This is true independent of which reference condition is used (i.e. MFR_h vs. MFR_{bp}). The differences between the calculated constant and variable velocity MFR's can be understood by considering the differences in terms of an equivalent shift in vapor pressure and ΔH_{vap} . To produce a thermogram under constant velocity conditions that is similar to the one with the actual velocity profile for a single component aerosol results requires a decrease in the ΔH_{vap} and an increase in the vapor pressure. For the example shown in Fig. 2 ($C_{\text{sat}}=5\mu\text{g}/\text{m}^3$), it was necessary to decrease ΔH_{vap} by ca. 15–20 kJ/mol (from 100 kJ/mol) and increase C_{sat} by ca. a factor of 1.8 to bring the constant velocity thermogram into agreement with the velocity profile ther-

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mogram. For smaller values of C_{sat} , somewhat smaller decreases in ΔH_{vap} and greater increases in C_{sat} appear to be necessary (ca. 10 kJ/mol and a factor of three for e.g. $C_{\text{sat}}=0.01 \mu\text{g}/\text{m}^3$). Thus, if an average velocity (or residence time) is used rather than the actual velocity profile, the vaporization enthalpy needed to match the model with measurements will be smaller than the actual value.

3.2 Influence of the denuder

As discussed above, the role of the denuder is to strip gas-phase molecules out of the air stream, thus leading to a decrease in the gas-phase concentration. As $C_{g,i}$ is reduced due to wall losses the particles will evaporate until such time as gas-particle equilibrium is re-established. To understand the influence of the gas stripping which occurs in the denuder, the MFR_{bp} has been calculated at T_{ref} for a single component aerosol as a function of the saturation vapor pressure. For typical thermodenuder conditions ($t_{\text{res}}=15$ s), the presence of the denuder section has a minimal influence on the calculated MFR_{bp} when $C_{\text{sat}} < 1 \mu\text{g}/\text{m}^3$ (Fig. 3a). However, for $C_{\text{sat}} > 1 \mu\text{g}/\text{m}^3$ the inclusion of the denuder leads to a decrease in MFR_{bp} below 1. For example, for $C_{\text{sat}}=10 \mu\text{g}/\text{m}^3$ $\text{MFR}_{bp} \sim 0.8$. For a given C_{sat} there is only a very small dependence on the total aerosol mass loading. There is, however, a noticeable dependence on the particle size (Fig. 3, inset). For a given C_{sat} and t_{res} , smaller particles have a lower MFR_{bp} than bigger particles. This is primarily a consequence of variations in both the non-continuum term, Γ , and the surface area-to-volume ratio with particle diameter. Additionally, the calculated MFR_{bp} (at T_{ref}) depends explicitly on the residence time in the denuder (Fig. 3b). Overall, it is found that the inclusion of the denuder section leads to evaporation of the particles, the extent of which depends on the compound vapor pressure, assumed evaporation coefficient, particle size and average residence time.

It is additionally important to consider how the denuder affects measurements made at elevated temperatures, where re-condensation is a concern. This has been explored

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by running calculations with the denuder section turned “on” and “off”. (On is the default condition.) Note that for the off condition the denuder remains as a cooling section but the gas-phase collection efficiency is set to 0. Here, the MFR_d values are compared in order to isolate the effect of re-condensation from further evaporation. Figure 4 shows

that the presence of the denuder section is most important for high loadings, which are typical of laboratory experiments. For ambient loadings (a few tens of $\mu\text{g}/\text{m}^3$ or less) the potential for re-condensation is found to be small, at least for the timescales considered here, which is consistent with the results of Huffman et al. (2008). This suggests that re-condensation may be more of a concern for laboratory measurements, which are commonly conducted using higher aerosol loadings (Sakurai et al., 2003). Why is this the case? At lower loadings, there is less total particle surface area available for re-condensation, which has the effect of slowing the condensation. Consider as an example a compound which has a $C_{\text{sat}}=100\ \mu\text{g}/\text{m}^3$. For this single component aerosol, when $C_{OA}=150\ \mu\text{g}/\text{m}^3$ the equilibrium gas-phase concentration is $C_{\text{gas}}=100\ \mu\text{g}/\text{m}^3$; when $C_{OA}=15\ \mu\text{g}/\text{m}^3$ C_{gas} still equals $100\ \mu\text{g}/\text{m}^3$. The gas-phase concentration has not changed but the particle mass (and surface area, assuming a fixed particle size) has decreased by a factor of 10 and thus the re-condensation rate is slower. However, if the time after the heated section is sufficiently long then re-condensation will always be a concern. The residence time between the thermodenuder and the analytical equipment should therefore be kept as short as possible. Note also that when the denuder is “off” the MFR_d still eventually goes to zero. This occurs when all particles have completely evaporated in the heated section and, since nucleation is not allowed in the model, there is no particle surface area available for re-condensation.

This balance between re-condensation and evaporation can be visualized more explicitly by examining the time-dependent output from the model at a given temperature, specifically using the particle radius as a metric (Fig. 5). As expected, those particles closest to the walls are affected most strongly, both in the heated section and the denuder section, due to their longer residence times compared to particles near the center of the tube (note that the temperature profile is assumed to be constant at all

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radial positions in the heater and denuder). Although two specific cases have been selected for consideration here (a high C_{sat} , high C_{OA} case and a low C_{sat} , low C_{OA} case), a larger set of runs (not shown) indicates that C_{OA} plays a more important role than C_{sat} in determining the influence of re-condensation.

Of additional interest, the calculations indicate that it is possible to have some particles completely evaporate while others retain some mass while transiting the thermodenuder, i.e. particle number losses are possible. This is a result of there being a radial velocity gradient. This evaporation-induced particle loss should not be confused with particle losses at elevated temperatures due to thermophoresis (which is not explicitly accounted for here), or with the enhancement of diffusion losses that results as particles shrink and become more diffusive. This result is consistent with the experimental results of Huffman et al. (2008), who showed number losses that increased as the initial particle size decreased. These results suggest that care must be taken in correcting thermodenuder experiments for particle number losses. Such corrections are best done using a “non-volatile” aerosol which is not subject to the evaporation-induced losses, as in Huffman et al. (2008).

The question of whether the equilibrium assumption is ever appropriate to use to interpret thermodenuder measurements has also been considered here. Here, “equilibrium assumption” specifically refers to the idea that the system (particles+gas) will equilibrate at the temperature of the heated section and remain in this state until some measurement (e.g. size, composition, etc.) is performed. It has previously been suggested that if a thermodenuder with sufficiently long residence time is used then the equilibrium assumption becomes valid (An et al., 2007). However, the cooling section and presence of the denuder means that the system will never emerge at the equilibrium condition of the heater temperature no matter how long the residence time. When the residence time in the heated section is increased, it is also increased by a proportional amount in the denuder section. As such, the influence of the denuder will be greater. High volatility compounds (ca. $C_{\text{sat}} > 10^2 \mu\text{g}/\text{m}^3$) may come to equilibrium on a reasonably short timescale (10's of seconds) in the heated section, but it is these

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high volatility compounds that are most sensitive to gas-stripping in the denuder. Low volatility compounds are not all that sensitive to the denuder section, however they will not reach equilibrium in the heated section in any reasonable (i.e. experimentally accessible) time period.

3.3 Influence of the thermodynamic properties of the aerosol components

Mass thermograms for single component aerosol with different saturation vapor pressures (C_{sat}) and a fixed ΔH_{vap} (Fig. 6a) have been calculated. As expected, the temperature which must be reached in the thermal denuder to cause complete evaporation of the particles varies inversely with vapor pressure. More specifically, the model indicates that there is a linear relationship between $\log(C_{\text{sat}})$ and $1/T_{50}$ (Fig. 6c) where T_{50} is the temperature where $\text{MFR}_{bp}=0.5$. This is similar to what was determined previously by Faulhaber et al. (2009); depending upon the assumed ΔH_{vap} , d_p , D_j , etc. quantitative agreement between the model and the Faulhaber et al. results can be obtained (Fig. 6c). (Note that this relationship breaks down somewhat at high C_{sat} if MFR_d is instead considered.)

The influence of the choice of ΔH_{vap} for a fixed C_{sat} on the calculated mass thermogram has been explored as well (Fig. 6b). Interestingly, for a fixed C_{sat} , T_{50} and ΔH_{vap} have a relationship that can be best described through a power law with $\Delta H_{\text{vap}}=a+b \times T_{50}^p$ (Fig. 6d). The parameters a and b are not unique as they depend on the assumed C_{sat} , C_{OA} , d_p , etc., and therefore they are not reported here. However, in general for low ΔH_{vap} small changes in ΔH_{vap} are predicted to have a large influence on the T_{50} while at high ΔH_{vap} comparably large changes are needed to cause even small changes in T_{50} (Fig. 6c). For example, if ΔH_{vap} is changed from 50 kJ/mol to 60 kJ/mol, T_{50} changes by more than 25°C (for $C_{\text{sat}}=1 \mu\text{g}/\text{m}^3$, $C_{OA}=50 \mu\text{g}/\text{m}^3$, $t_{\text{res}}=15 \text{ s}$ and $d_p=300 \text{ nm}$). This is equivalent to an order of magnitude change in C_{sat} . Clearly, results from thermodenuder studies must be considered in the context of temperature-dependent volatilities and not only in terms of the volatility of the various components

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near room temperature (where aerosol yield experiments are typically conducted). Improved characterization of ΔH_{vap} for atmospherically-realistic compounds and mixtures is critically needed to interpret ambient TD data quantitatively.

3.4 Influence of physical properties: size and diffusion

5 The influences of particle size and mass loading on the calculated T_{50} were both investigated. At low mass loadings, the T_{50} decreased monotonically with particle diameter (Fig. 7). At higher loadings the T_{50} decreased with d_p for large diameters, but became relatively insensitive to changes in particle diameter for small d_p . This is somewhat different than was found for the room temperature (i.e. denuder-only) calculations above,
10 where only a weak dependence on mass loading was found. This difference arises in large part because the particle number concentration increases with C_{OA} (for a fixed d_p), and each particle has a smaller gas-phase volume available for evaporation (equal to $1/N_p$). As temperature is increased and evaporation occurs, the gas-phase will become saturated more rapidly at higher mass loadings due to the smaller available volume per particle. Consequently, the magnitude of mass loss for a given temperature
15 will scale inversely with loading, which is observed as an increase in the T_{50} with C_{OA} (for a given d_p). This is consistent with the results of Faulhaber et al. (2009). This loading effect does not apply in the same way to the room temperature (denuder-only) calculations because the driving force for evaporation is actually removal of gas-phase
20 molecules by the denuder. The gas-phase in the denuder will not become saturated no matter how small the volume per particle, and thus there is a negligible dependence of MFR(25°C) on C_{OA} . Additionally, it was determined that the general form of the dependence of T_{50} on d_p was independent of ΔH_{vap} , although ΔH_{vap} does have an influence on the absolute T_{50} values.

25 The sensitivity of the calculations to the assumed gas-phase diffusion coefficient was also determined (Fig. 8). As expected, T_{50} increases as D_i decreases. The general nature of the relationship between D_i and T_{50} is essentially independent of d_p , mass loading and ΔH_{vap} , although the absolute range over which T_{50} varies does depend on

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these variables. The D_i vs. T_{50} relationship is non-linear, with a higher sensitivity for smaller D_i . It is difficult to come up with a generally applicable uncertainty estimate based on the uncertainty in D_i because this will depend on the specific conditions (d_p , C_{OA} and ΔH_{vap}). However, if it is assumed that D_i can be known to within $\pm 20\%$, it can be seen in Fig. 8 that the associated variability in T_{50} ranges from much less than a degree up to a few degrees.

3.5 Multi-component aerosol

The model which has been developed is not limited to single-component aerosols, but can be used to describe the evaporation behavior of individual components from a multi-component aerosol. As such, the model may find use in interpreting both laboratory thermodenuder measurements of primary or secondary organic aerosol or field observations. As an example of the general utility of the model for use with multi-component aerosol, a theoretical mass thermogram has been calculated for a 7-component aerosol with compounds having saturation concentrations ranging from 10^{-3} to $10^3 \mu\text{g}/\text{m}^3$. For simplicity, in this example it has been assumed that the aerosol contains equal parts by mass of each component at the initial equilibrium condition and also that each compound has the same ΔH_{vap} ($=90 \text{ kJ/mol}$). Figure 9 shows the calculated total mass fraction remaining for this theoretical multi-component aerosol for the three different reference conditions (i.e. bypass, denuder and heated tube-only).

As expected, the more volatile components begin to evaporate from the particles at lower temperatures than the less volatile components. Because the aerosol here is comprised of compounds with a distribution of vapor pressures, the overall mass thermogram extends over a wide range of temperatures and is not nearly as sharp as that for the individual components (Fig. 9).

The calculated MFR_{bp} suggests that there should be mass loss observed at ambient temperature due to evaporation of the higher-volatility components in the denuder section, if such compounds constitute a significant fraction of the sampled aerosol. Additionally, at high temperatures MFR_{bp} and MFR_h give similar results. This can be

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understood in the context of what is shown in Fig. 5. At higher temperatures, the “high-volatility” material has already evaporated. Once that occurs, the denuder section primarily serves to limit re-condensation and, at low loadings, re-condensation is not a major concern (at least on the timescales considered here, as discussed above).

3.6 Comparison with observations: testing the model

The model has been tested by comparing with the experimental observations of Faulhaber et al. (2009), where the mass thermograms of single-component particles with known temperature-dependent vapor pressures were determined, specifically for butanedioic, hexanedioic and decanedioic acids (Fig. 10). There has been some disagreement in the literature over the exact temperature-dependent vapor pressures of the compounds used by Faulhaber et al. (e.g. Bilde et al., 2003; Chattopadhyay and Ziemann, 2005; Cappa et al., 2007). The observations have therefore been considered in the context of the thermodynamic parameters reported by both Chattopadhyay and Ziemann and Cappa et al. individually, as well as by using average values. The model inputs used were $d_p=200$ nm, $C_{OA}=150\text{ }\mu\text{g/m}^3$, $Q=0.6$ slpm, $T_{\text{ref}}=25^\circ\text{C}$ and $\gamma_e=1$. Because the Cappa et al. vapor pressures are lower than the Chattopadhyay et al. vapor pressures, for these compounds there is a general tendency for more mass to remain at a given temperature when the Cappa et al. vapor pressures are used. Additionally, there is some tendency for the measured thermograms to be less steep than the calculated thermograms. Nonetheless, it is evident that the model qualitatively captures the observed TD behavior for each of the dicarboxylic acids considered, and when the average vapor pressures and ΔH_{vap} ’s are used semi-quantitative agreement is obtained, thereby providing confidence in our model.

3.7 The evaporation coefficient

It is generally accepted that for individual organic compounds the evaporation coefficient is unity (or very close) (Kulmala and Wagner, 2001) and, for comparison, the

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evaporation coefficient for water is similarly large (values range from ca. 0.3 to 1) (Li et al., 2001; Winkler et al., 2004; Smith et al., 2006). An evaporation coefficient less than one indicates that there is strong barrier to the formation of the “critical” surface species that precedes evaporation (Davidovits et al., 2006). (Recall that the evaporation coefficient is defined as a deviation from the theoretical maximum evaporation rate. That theoretical maximum is directly proportional to the vapor pressure, which is an equilibrium property describing the energetic difference between the vapor and bulk liquid, and thus is independent of the surface.) However, recently it has been suggested that the evaporation coefficient, γ_e , for complex organic aerosol, specifically lubricating oil and secondary organic aerosol from the α -pinene+O₃ reaction, is significantly less than one ($0.001 < \gamma_e < 0.01$) (Grieshop et al., 2007, 2009). If γ_e is small, this would have the effect of decreasing the evaporation rate for a compound with a given C_{sat} value. For example, a compound with $C_{\text{sat}} = 100 \mu\text{g}/\text{m}^3$, which is predicted to evaporate significantly in the thermodenuder at room temperature, would not be observed to evaporate significantly for typical experimental timescales if $\gamma_e < 0.01$. For systems where the temperature dependent vapor pressures of the individual aerosol components of a multi-component mixture are known a priori, the model developed here can be used to determine the evaporation coefficient (although there may be some challenges associated with differentiating the effects of non-ideal solution behavior, e.g. Cappa et al. (2008), and evaporation coefficients that differ from unity). However, in order to determine temperature dependent vapor pressures for unknown systems, it is necessary to specify some value of γ_e and then to work within this constraint. Further work is certainly needed to properly constrain the probable value (or values) of γ_e for atmospheric aerosols.

4 Conclusions

A new model of multi-component aerosol evaporation in a thermodenuder has been developed. Unlike previous models, separate heating and denuder sections are ex-

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5 plicitly accounted for as is the velocity profile through the denuder tube. As expected, higher temperatures are required to achieve equivalent amounts of evaporation for low volatility vs. high volatility components. A relationship between the saturation concentration and temperature has been established ($\log C_{\text{sat}} \propto 1/T_{50}$) and found to be consistent with that reported by Faulhaber (2009). The influence of ΔH_{vap} on the calculated mass thermograms has been shown to be significant; a power law was determined to best describe the relationship between temperature and ΔH_{vap} for a fixed C_{sat} . For low ΔH_{vap} values (<ca. 100 kJ/mol) the calculated mass thermogram is very sensitive to the chosen ΔH_{vap} . Reasonable agreement is found between the calculated and observed mass thermograms for a few low-volatility dicarboxylic acids (Faulhaber et al., 10 2009), demonstrating that the model can be used for quantitative analysis of thermodenuder observations.

Importantly, it has been demonstrated that the inclusion of the adsorbent denuder section is crucial to understanding the behavior of “semi-volatile” aerosol (1 $\mu\text{g}/\text{m}^3 < C_{\text{sat}} < 1000 \mu\text{g}/\text{m}^3$) in the thermodenuder. The presence of the denuder engenders loss of particle mass as a result of evaporation of particles as a response to stripping of the gas-phase molecules by the denuder. For lower volatility components the denuder has minimal influence at room temperature because the evaporation rates of these compounds from the particles are so low. However, the denuder still serves an important purpose in that it helps to limit re-condensation of the material that had evaporated in the heated section. The extent to which re-condensation influences the calculations appears to depend most acutely on the assumed loading with a greater influence found at high loadings. Additionally, it has been shown that the assumption that equilibrium can be reached in the thermodenuder at long residence times is incorrect. 20 The model which has been developed here can be used to provide quantitative understanding of aerosol volatility measurements of single and multi-component aerosol made using thermodenuders.

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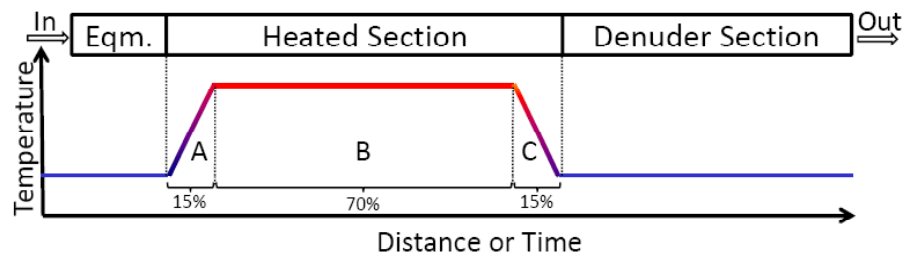


Fig. 1. Schematic of the thermodenuder model. Note that the temperature changes in the heated section take place over a distance. The heating zone is indicated by “A”, the hot zone by “B” and the cooling zone by “C”.

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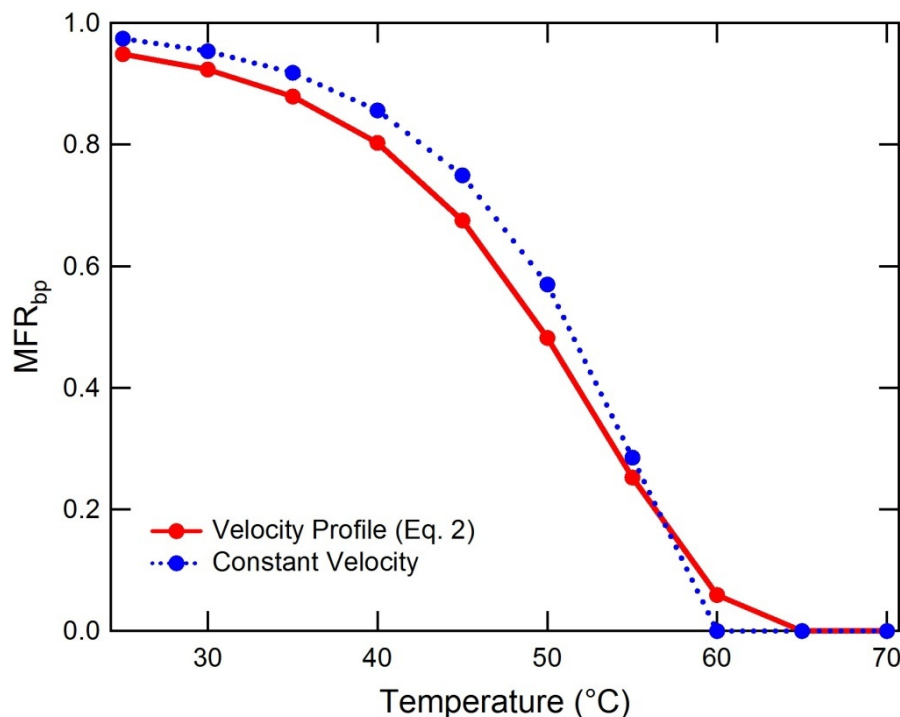


Fig. 2. The mass fraction remaining (referenced to the bypass, i.e. MFR_{bp}) is shown as a function of thermodenuder temperature. The solid red curve shows the case where the laminar flow velocity profile in the thermodenuder is explicitly considered and the dotted blue curve when a flat velocity profile is assumed. The calculations assume a single-component aerosol with $d_p=200$ nm, $C_{sat}=5$ $\mu\text{g}/\text{m}^3$, $C_{OA}=100$ $\mu\text{g}/\text{m}^3$, $\gamma_e=1$, and $t_{res}=16$ s.

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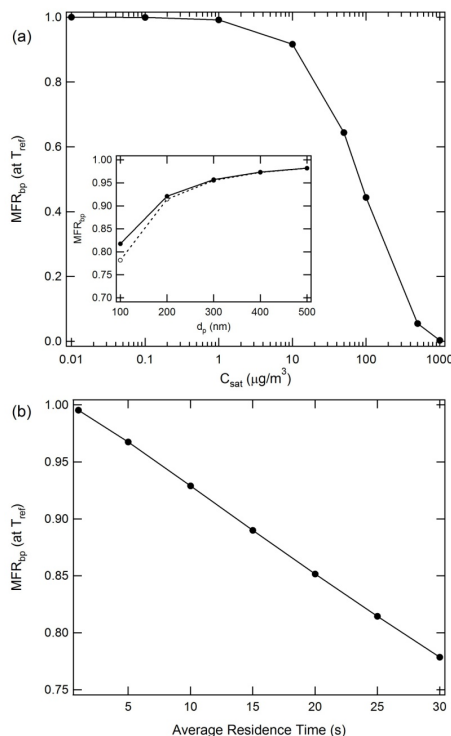


Fig. 3. (a) Calculated mass fraction remaining (referenced to the bypass) at 25°C for single-component particles shown as a function of C_{sat} ($d_p=200$ nm, $C_{\text{OA}}=50$ µg/m³). (inset) Calculated MFR_{bp} at 25°C as a function of particle diameter for $C_{\text{sat}}=10$ µg/m³ at two different aerosol mass loadings, 5 µg/m³ (●) and 150 µg/m³ (○). (b) Calculated MFR_{bp} at 25°C as a function of the residence time in the denuder ($C_{\text{sat}}=10$ µg/m³, $d_p=200$ nm and $C_{\text{OA}}=150$ µg/m³).

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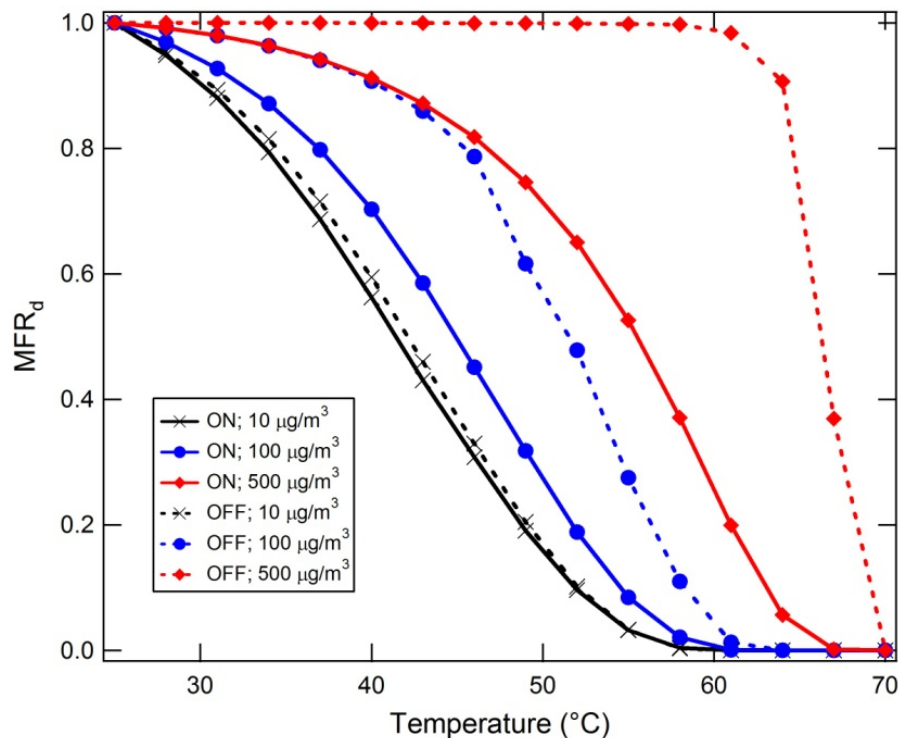


Fig. 4. The mass fraction remaining is calculated for when the denuder is assumed to be “on” (solid lines) or “off” (dashed lines) for various C_{OA} assuming $C_{sat}=10\text{ }\mu\text{g/m}^3$, $\Delta H_{vap}=90\text{ kJ/mol}$, $t_{res}=16\text{ s}$, $D_p=200\text{ nm}$ and $\gamma_e=1$. The C_{OA} used were $10\text{ }\mu\text{g/m}^3$ ($\times$), $100\text{ }\mu\text{g/m}^3$ ($\bullet$) and $500\text{ }\mu\text{g/m}^3$ ($\blacklozenge$). Note that MFR_d is used here, i.e. the mass fraction remaining relative to the aerosol after having passed through the thermodenuder at T_{ref} .

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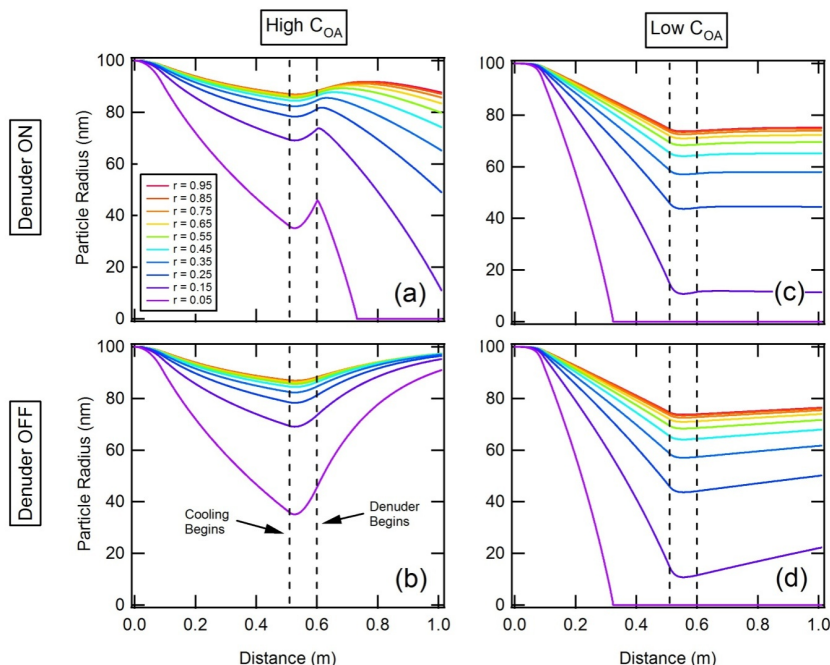


Fig. 5. The modeled variation in particle radius is shown as a function of the distance along the thermodenuder. The different curves in each panel correspond to particles that are closer to/further from the thermodenuder walls (line colors indicate the relative distance of that bin from the wall). Panels aligned vertically are for the same C_{sat} while panels aligned horizontally have the same denuder state (either “on” or “off”). The left panels (a and b) are for $C_{sat}=100\text{ }\mu\text{g}/\text{m}^3$ at $T_d=35^\circ\text{C}$, $C_{OA}=150\text{ }\mu\text{g}/\text{m}^3$ and $\Delta H_{vap}=60\text{ kJ}/\text{mol}$ while the right panels (c and d) are for $C_{sat}=1\text{ }\mu\text{g}/\text{m}^3$ at 60°C , $C_{OA}=15\text{ }\mu\text{g}/\text{m}^3$ and $\Delta H_{vap}=120\text{ kJ}/\text{mol}$. The top panels (a and c) had the denuder “on” and the bottom panels (b and d) had the denuder “off”. In all cases $t_{res}=15\text{ s}$ and $\gamma_e=1$. The vertical dashed lines indicate the point where the cooling begins (left) and the denuder section begins (right).

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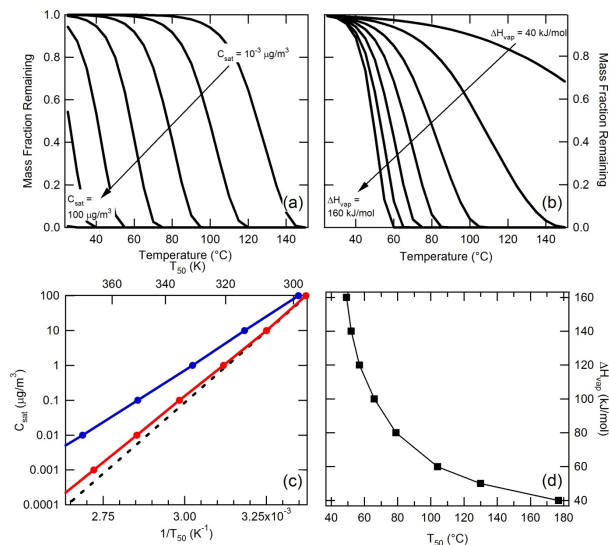


Fig. 6. (a) The calculated mass fraction remaining (MFR_{bp}) for particles passed through a thermal denuder is shown for different values of C_{sat} , ranging from $C_{sat}=0.01$ to $100 \mu\text{g}/\text{m}^3$. Here, it was assumed that $d_p=300 \text{ nm}$, $t_{res}=15 \text{ s}$, $\Delta H_{vap}=120 \text{ kJ}/\text{mol}$, $C_{OA}=50 \mu\text{g}/\text{m}^3$ and $\gamma_e=1$. (b) Same as (a), but where the ΔH_{vap} values were varied from 40 to 160 kJ/mol (in 20 kJ/mol steps) for $C_{sat}=1 \mu\text{g}/\text{m}^3$. (c) The calculated T_{50} is shown as a function of C_{sat} and (d) as a function of ΔH_{vap} ($C_{sat}=1 \mu\text{g}/\text{m}^3$, $d_p=300 \text{ nm}$). For (c), the calculations used $\Delta H_{vap}=120 \text{ kJ}/\text{mol}$ and $d_p=300 \text{ nm}$ (blue line) or $\Delta H_{vap}=150 \text{ kJ}/\text{mol}$ and $d_p=200 \text{ nm}$ (red line). Note that T_{50} values in (c) are in K. The experimental C_{sat} vs. $1/T_{50}$ relationship determined by Faulhaber et al. (2009) is shown for reference (dashed line). A MW of 150 g/mol was assumed to convert vapor pressure to C_{sat} .

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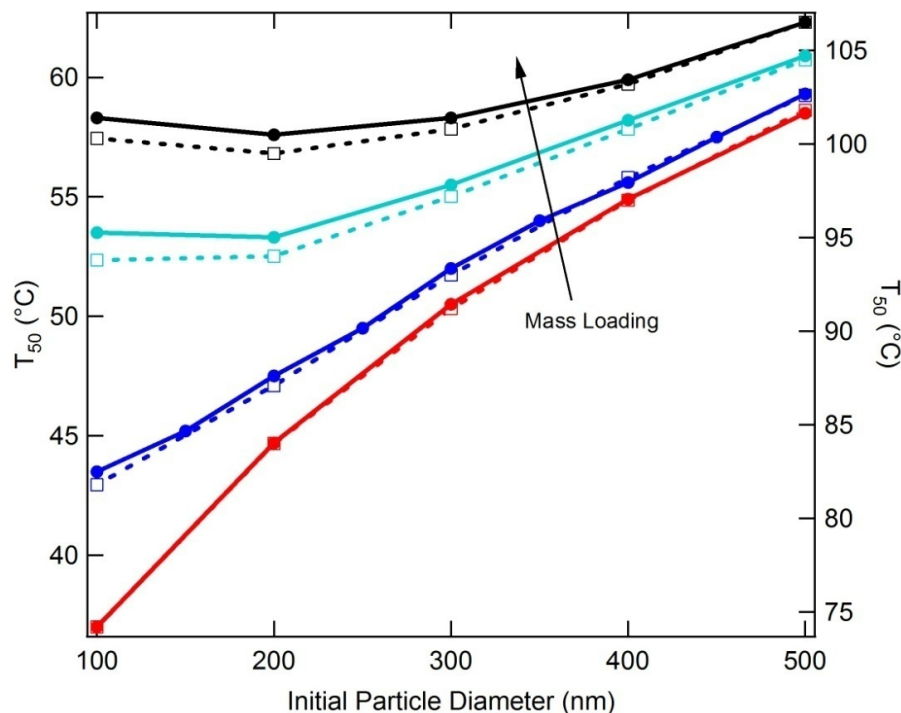


Fig. 7. Calculated dependence of T_{50} on the initial particle diameter. The different color lines correspond to different aerosol mass loadings ($5 \mu\text{g}/\text{m}^3$, $50 \mu\text{g}/\text{m}^3$, $150 \mu\text{g}/\text{m}^3$ and $250 \mu\text{g}/\text{m}^3$). The saturation concentrations used were either $C_{\text{sat}}=5 \mu\text{g}/\text{m}^3$ (solid lines, left axis) or $C_{\text{sat}}=0.1 \mu\text{g}/\text{m}^3$ (dashed lines, right axis). For these calculations, $\Delta H_{\text{vap}}=100 \text{ kJ}/\text{mol}$, $D_i=3.5 \times 10^{-6} \text{ m}^2/\text{s}$ and $t_{\text{res}}=15 \text{ s}$.

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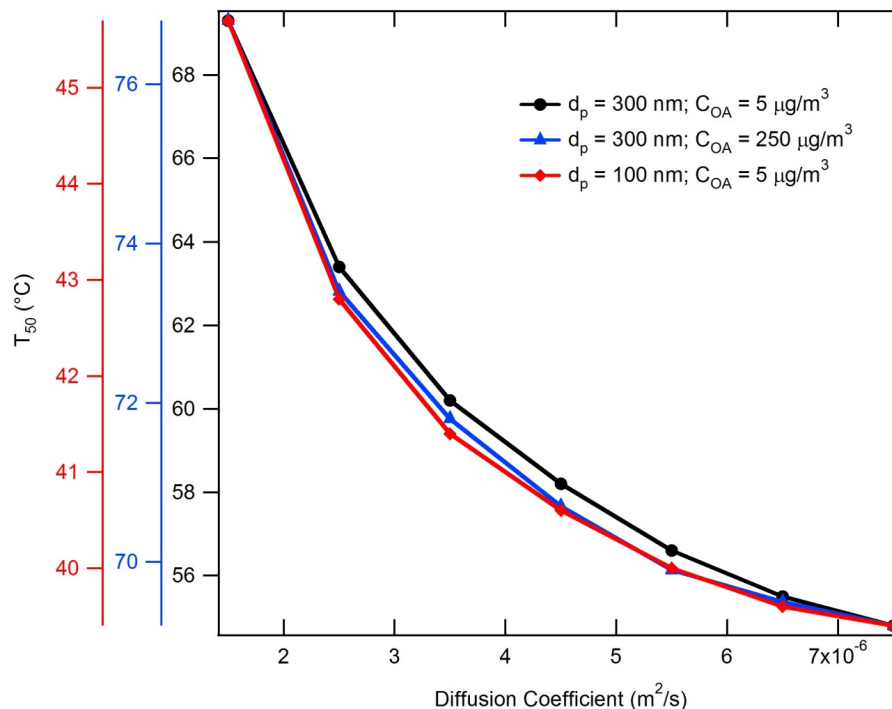


Fig. 8. Calculated dependence of T_{50} on the diffusion coefficient. The line colors correspond to the axis colors and were for (black) $d_p=300$ nm and $C_{OA}=5 \mu g/m^3$, (blue) $d_p=300$ nm and $C_{OA}=250 \mu g/m^3$ and (red) $d_p=100$ nm and $C_{OA}=5 \mu g/m^3$. In all cases, $\Delta H_{vap}=75$ kJ/mol, $C_{sat}=5 \mu g/m^3$ and $t_{res}=15$ s. The general form of the relationship between T_{50} and D_i is relatively insensitive to the specific conditions (e.g. ΔH_{vap} , D_p , C_{OA}), although the absolute range over which T_{50} varies depends on these parameters.

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Interactive Discussion



A model of aerosol evaporation kinetics in a thermodenuder

C. D. Cappa

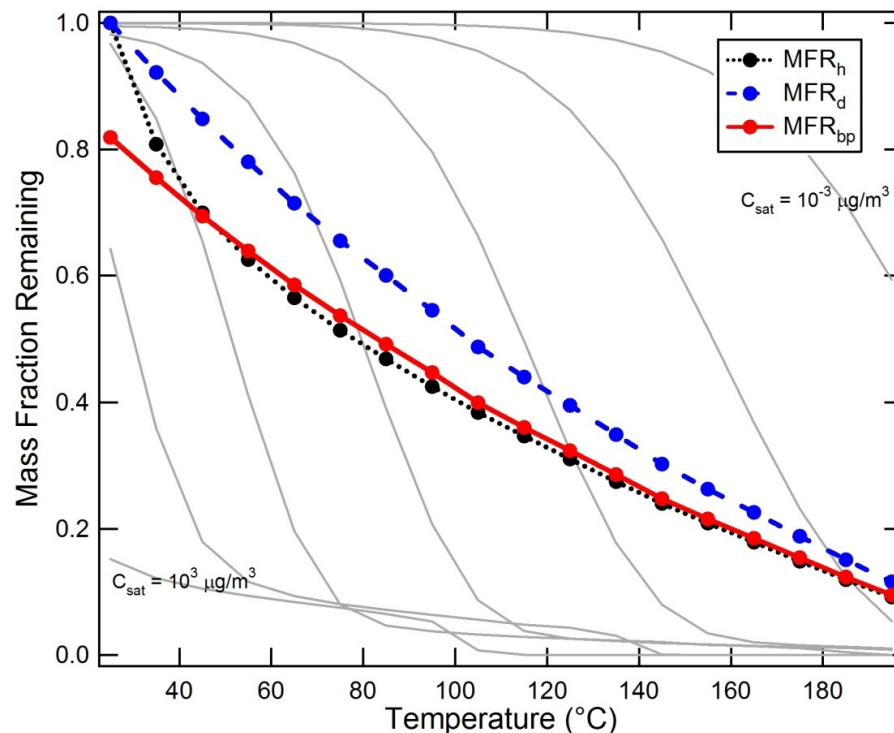


Fig. 9. Calculated mass fraction remaining for an equimass mixture of compounds where the reference state is the bypass (solid red line), denuder (dashed blue line) or heated tube-only (dotted black line). The C_{sat} values ranged from 10^{-3} to $100 \mu\text{g}/\text{m}^3$. Mass thermograms are also shown for the individual compounds comprising the aerosol as they evaporate from the mixture (thin gray lines). Here, $\Delta H_{\text{vap}}=90 \text{ kJ}/\text{mol}$, $\gamma_e=1$, $t_{\text{res}}=15 \text{ s}$, $C_{\text{OA}}=21 \mu\text{g}/\text{m}^3$ and $d_p=300 \text{ nm}$.

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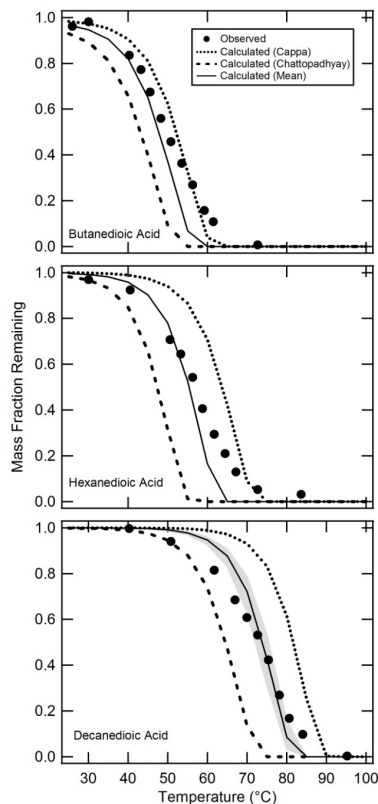


Fig. 10. Calculated mass fraction remaining (referenced to bypass) for butanedioic, hexanedioic and decanedioic acid compared to observations by Faulhaber et al. (2009). The thermodynamic parameters (C_{sat} and ΔH_{vap}) used are from Cappa et al. (2007) (dotted), Chattopadhyay and Ziemann (2005) (dashed) or the average of the two (solid). The model was run using $d_p=200$ nm, $t_{\text{res}}=16$ s, $\gamma_e=1$ and $C_{\text{OA}}=150$ $\mu\text{g}/\text{m}^3$. For decanedioic acid the gray region shows the range for 100 $\mu\text{g}/\text{m}^3 < C_{\text{OA}} < 200$ $\mu\text{g}/\text{m}^3$.

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