

Interactive comment on “A model of aerosol evaporation kinetics in a thermodenuder” by C. D. Cappa

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Received and published: 2 February 2010

The manuscript describes modeling of organic aerosol dynamics in thermodenuders. Thermodenuders are widely used to study laboratory and ambient aerosol thermodynamic properties and thus are of great interest for the research community studying semi-volatile aerosol. Unfortunately, this manuscript has a number of significant errors, which invalidate most of its conclusions. These are enumerated below.

First, the author uses an erroneous assumption that the walls in the cooling section do not act as a sink for gaseous organic species (p. 2756, lines 2-3: “Note that for the ‘off’ condition the denuder remains as a cooling section but the gas-phase collection efficiency is set to 0.”). In reality, any gaseous substance, whose vapor pressure is higher

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than the saturation vapor pressure at the temperature of the tube wall, will condense onto the wall. This effect is routinely observed when sampling warm, humid outdoor air into an air-conditioned room: transfer lines and instruments become flooded with water. In fact, due to this process, we have observed organic coatings forming on the walls of our sampling tubing downstream of a TD when working with dicarboxylic acid aerosols. Therefore, for pure substances, the cooling section should have a boundary condition set to the saturation vapor concentration (C_{sat}) of the species at the temperature of the wall. For mixtures, the boundary condition for each compound should be the saturation pressure (P_{sat}) corresponding to the wall temperature, corrected for the molar fraction of the compound in the mixture. This boundary condition is critical because it is what leads the aerosol-vapor system to equilibrate, contrary to the conclusion of the author. Further, this also illustrates why a denuder should not be incorporated in the cooling section of a TD employed to estimate aerosol thermodynamic properties; the denuder will prevent the system from equilibrating at the cooling section temperature, and thus provides a poorly characterized endpoint for inferring thermodynamic properties.

The erroneous boundary condition naturally leads to the author's model predicting a strong time-dependent re-condensation effect; that is, whatever has evaporated in the heated section will return back into the particle phase when the temperature drops back to T_{ref} given sufficient time. This state of affairs is invoked to suggest the need for a denuder. However, as discussed above, this is not what happens. As can be shown both by modeling and by empirical observation, heat transfer to the walls is rapid. Since the processes of heat and mass transfer scale with the corresponding diffusivities (and most often the ratio of these, the Lewis number, is of order 1), the cooling and mass transfer to the walls occur on comparable time scales. Therefore, the concentration in the gas phase should follow the temperature profile, such as the one shown in Fig.1. Of course, the lower the diffusion coefficient of the species relative to the thermal diffusivity, the more the concentration profile will lag relative to that of the temperature. This will allow more time for the gas to condense back onto the particles. However, the condensation rate to the particles will also be proportionally slower, in

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fact by the same ratio, because both processes (condensation to the walls and onto the particles) depend on the diffusion coefficient in exactly the same way (Eq.1 and 4).

Given the above, the estimates of re-condensation in the cooling section reported in this manuscript are most probably grossly over-estimated. At the very least, any conclusions based on the approach used by the author are not warranted and need to be re-evaluated using correct boundary conditions. We have not found any significant re-condensation in the TD cooling section using a more complete model (Saleh et al., 2008) than the one presented in this manuscript. Our model accounts for parabolic flow profile, but also solves for heat transfer and is particle size-resolved. According to our simulations, there is no appreciable re-condensation effect if no absorber is used in the cooling section. The absorber, on the other hand, may cause a substantial negative bias in the final aerosol volume, if long residence times are used.

There are other problems with the manuscript, which are discussed below.

Figure 4 shows MFR (mass fraction remaining) at different mass loadings and is used by the author to conclude that the use of an absorber is very important at high aerosol concentrations (p.2759 "Figure 4 shows that the presence of the denuder section is most important for high loadings, which are typical of laboratory experiments."). Figure 4, however, only compares the cases when the denuder is used or not in the cooling section (the "on" and "off" cases, respectively). The "off" case is most probably biased high due to the re-condensation. The "on" case is assumed to be correct or to have a smaller error, which is probably not the case. In fact, Figure 3 demonstrates that the denuder can absorb more than $50 \mu\text{g}/\text{m}^3$ of material causing a strong negative bias for semi-volatile aerosols even at room temperature. At higher gas concentrations originating from the heated section this bias will be even larger, due to a stronger driving force (concentration gradient in the first term of Eq.1). The magnitude of this negative bias is not shown in Figure 4. Therefore, the conclusion about the importance of the denuder at any aerosol concentration is not supported by the figure and is, actually, wrong.

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The conclusion that the denuder is most important for high loadings is also questionable. It is based on the larger deviation between the "on" and "off" cases at higher concentrations. First of all, as discussed above, the MFR for the "off" case are most probably grossly overestimated, because the condensation to the walls was erroneously switched off. Secondly, no proof is given that the negative bias due to the gas stripping by the denuder would not increase at higher aerosol concentrations. In fact, Figure 5 shows that for the "on" case most trajectories demonstrate a significant decrease in particle size, such that at the end of the denuder the particle size is well below the size at the end of the heated section. This must lead to a strong negative bias in the "on" case. The conclusion about the importance of the denuder at high C_{OA} appears to be the exact opposite to what the model indicates: the denuder introduces a larger bias at higher C_{OA} than at the low C_{OA} . Granted, the author acknowledges that Figure 5 is in effect comparing apples to oranges: a high C_{OA} / high C_{sat} compound vs. low C_{OA} / low C_{sat} one, i.e. there are two competing factors in play: C_{OA} and C_{sat} . The only reason why the author picks C_{OA} over C_{sat} as the most important factor in re-condensation is: "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." It is not clear why the data supporting this is not shown, while the negative bias due to the denuder is glossed over.

On p.2760 the author states that "When the residence time in the heated section is increased, it is also increased by a proportional amount in the denuder section." This asserted proportionality is arbitrary, and the ensuing analysis is highly misleading. In reality, one may design the cooling section as needed. For example, in our previous studies (Saleh et al., 2008, 2009), the sampling line out of the TD served as a cooling section and, due to relatively fast wall heat and mass transfer, required a residence time about 10% of that used in the author's model.

On p. 2761 and the related statement in the conclusions about the equilibration times: "Low volatility compounds are not all that sensitive to the denuder section, however they

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will not reach equilibrium in the heated section in any reasonable (i.e. experimentally accessible) time period.” The author gives no justification for the second part of the statement. The statement and the corresponding conclusions about the equilibration times are highly misleading because they are not qualified by the specific conditions modeled by the author, and thus falsely give an impression of universality. In reality, the equilibration time depends not only on the C_{sat} , but also on the concentration of aerosol and its size distribution, which is clear from Eq. 1.

The statement in the conclusions “Unlike previous models, separate heating and denuder sections are explicitly accounted for as is the velocity profile through the denuder tube” exaggerates the achievements of the presented model. We have previously described a size-resolved model for aerosol evolution in wet annular and flat denuders that takes into account velocity profile, hygroscopic growth and transfer of the gas species to and from the particles and the walls (Khlystov et al., 2009). An adaptation of this model to thermodenuders, which includes heat exchange with the walls, was used to test the effect of re-condensation and an absorber in the cooling section (Saleh et al., 2008). Unlike our model, the one presented in this manuscript assumes that the radial temperature profile is constant (p.2759 line 29) and works only with monodisperse aerosol. The size distribution of particles may have a profound effect on the evaporation/condensation rates because of the strong dependence of evaporation rate on particle size. Radial temperature gradients are extremely important too. In the transition regions (cold to hot and hot to cold) the temperature gradient is the leading cause of different evaporation/condensation rates experienced by particles at different distances from the wall. These differences are critical for the evolution of the particle sizes and gas phase concentrations in the system. Unfortunately, these radial gradient effects in the transition region are ignored in the model presented in this manuscript (the temperature is assumed to linearly increase or decrease with axial distance, while being uniform in the radial direction). Since the presented model does not take into account radial heat transfer, the only source of radial concentration gradient in the heated section is due to the differences in the time particles spent there. The author does

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not indicate how strong these radial gaseous concentration gradients are and whether they are significantly larger than the axial diffusion (the equations indicate an implicit assumption that the axial diffusion is negligible).

Results presented in Figure 5 also raise some questions about the performance of the model, though I may be missing some critical information to make an accurate judgement. The problem is with an apparent break-down of mass conservation in the heated part of the system. The information presented in the figure caption is somewhat confusing, but is sufficient to calculate the difference in C_{sat} at the temperatures in the entrance (T_0) and in the heated section (T_h). The amount of material needed to saturate the air is $dC = C_{sat}(T_h) - C_{sat}(T_0)$. Since the author uses monodisperse aerosol assumption, one can calculate to which size particles need to evaporate to saturate the air at T_h . The new size should be: $r = r_0(1 - dC/C_0)^{1/3}$, in which r_0 is the initial particle size and C_0 is the initial aerosol mass concentration (given in the caption as C_{OA}). For the high C_{OA} case ($dC = 53 \mu\text{g}/\text{m}^3$, $C_0 = 150 \mu\text{g}/\text{m}^3$) the final aerosol size should be 86.5 nm. Most of the trajectories seem to satisfy this. The few closest to the walls, however, show evaporation to significantly smaller sizes. The question is: since there is no absorption by the walls in the heated section, where does this evaporated material go? If the evaporated material remains in the gas phase, the gas should become supersaturated. Yet, in the model particles continue to evaporate. The low C_{OA} case ($dC = 1 \mu\text{g}/\text{m}^3$, $C_0 = 15 \mu\text{g}/\text{m}^3$) demonstrates even stronger discrepancy: the final size should be 97.7 nm, yet all of the trajectories end up at significantly smaller sizes. I apologize if I miss something here, but I feel this phenomenon needs to be explained.

Other questions about the model: As the second reviewer pointed out, the boundary conditions need to be clearly described in the methods section (currently, some of them can be found only in the results section). No sensitivity analysis is given for the model performance with respect to the number of concentric cylinders, which are used to calculate radial mass transfer. In fact, their number is not given.

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In summary, I believe that while this manuscript tackles an important problem, its conceptual errors lead to an erroneous picture of transport phenomena in thermodynamic systems, with important practical implications for ongoing studies of aerosol thermodynamics.

Acknowledgements

I thank Dr. Alan Shihadeh and Rawad Saleh for their contribution to this review.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 2749, 2009.