

We thank the reviewers for their comments, most of which are central to the subject of thermodynamic modeling and measurements, and have thus added to the ongoing discussion and helped us improve the manuscript. Below are detailed responses to the reviews, with the reviewers' comments indicated in italics.

Response to Christopher Cappa

The replies are numbered according to the numbering of Dr. Cappa's comments.

1.

The derivation presented in this comment is erroneous. In equation (5), $C_g^* = C_g / C_{sat}$ can *not* be replaced with $C_{sat,0} / C_{sat}$ because C_g varies continuously during evaporation ($C_g = C_{sat,0}$ *only* at $t = 0$), thus the cancellation of $C_{sat,0}$ and the subsequent conclusion that dC_g^* / dt^* depends on ΔH is not valid. ΔH determines the difference between $C_{sat,0}$ and C_{sat} , but this has no effect on the evolution of C_g^* in the TD, as described in sections 2.2 and 4.3. Plots of C_g^* profiles with different ΔH values all lay on the same line; the evolution of the dimensionless vapor concentration truly does not depend on the thermodynamic properties of the aerosol.

2.

Thermodynamic properties are added in the revised manuscript.

3.

Point is well taken, (=) is replaced with (\approx) in equation (9).

We should note that the approximation in equation (9) is only employed to simplify the interpretation of experimental results, and it bears no significance on the validity of the theoretical analysis or the conclusions. This approximation (between 25 C and 40 C) is explicitly stated to be valid for the dicarboxylic acids in this study in line 10 p. 2942, and is not meant to be generalized.

4.

As described in section 4.1, equilibration time is a function of the product of the total number concentration and the condensation sink diameter ($N_{tot} d_{cs}$). This is technically referred to as the "aerosol length" (e.g. in William Hinds' classic text) or sometimes as "particle diameter concentration", and just like the "mass loading", it can be readily inferred from the particle size distribution. We are aware that "mass loading" is widely used in the community. We agree that the product of the number concentration and particle diameter can be easily found from the mass concentration and particle size. However, by explicitly using the term "particle length",

i.e. the sum-product of number concentration and particle diameter, we wanted to attract reader's attention to the fact that, indeed, it is not controlled by a single parameter, such as particle size, number concentration or particle mass. It is controlled by a combination of the two parameters, most easily expressed by $N_{tot} d_{cs}$. Because "aerosol length" is not as commonly used, we tell the reader that it is a property of the "size distribution" in line 23 p. 2939 and line 6 p. 2943. We also agree that if equilibrium is not reached in the thermodenuder, i.e. if the system is still in a transitory state, one must use a kinetic model to interpret the results.

5.

See #12

6.

The dimensional analysis presented in section 2.2 shows clearly that equilibration is not a function of C_{sat} . To recap, higher C_{sat} increases evaporation rate, but also increases the amount of evaporation needed to approach phase equilibrium, in such a manner that the two effects exactly cancel. We believe that comparing experimental equilibration time scales of adipic acid and pimelic acid provide adequate illustration. There is no reason why we did not choose azelaic and succinic acids instead, nor is there a reason to believe that having chosen those would have changed the results. The ratios of C_{sat} of azelaic, adipic, pimelic, and succinic acids at 40 C are approximately 1 : 2 : 6 : 9 (Saleh et al 2008, 2009, 2010), with all of them lying within an order of magnitude. According to Riipinen et al. (2010), for adipic acid, increasing the TD temperature from 24 C to 30 C, which corresponds to a factor of 3 increase in C_{sat} , results in a factor of 6 increase in equilibration time (Figure 2 in Riipinen et al. 2010). So, if our theoretical findings were wrong, and C_{sat} had an effect on equilibration time in the manner put forward by Riipinen et al., it would have shown in the experimental results. We have also added a figure (Figure 6 in the revised manuscript) that demonstrates that a three orders of magnitude difference in C_{sat} has no effect on the equilibration time.

With regards to the mixture, it is true that the "average" C_{sat} does not differ much from that of adipic and pimelic acid. However, the purpose of mixing the acids was not to obtain an aerosol with different C_{sat} , but to show that the suppression of C_{sat} of individual compounds in the mixture has no effect on equilibration time.

7.

Figure captions are changed in the revised manuscript.

8.

The colors/symbols used in Figure 5 correspond to the same colors/symbols in Figures 2 and 4. This is made clearer in Figure 5 caption in the revised manuscript.

ΔC_{max} was obtained experimentally for all cases. All experiments had measurements at equilibrium, as is apparent from the time evolution of aerosol concentration (Fig.2), except one experiment performed with adipic acid at low aerosol length (or, for a given size distribution, lower total concentration, Figure 2). For this experiment, ΔC_{max} was obtained from other experiments performed with adipic acid which had measurements at equilibrium. This is made clearer in section 4.1 in the revised manuscript.

9.

It is true that the change in aerosol mass concentration, *both* in the heated and cooling section of the TD, depends on C_{sat} , unlike the equilibration time in the heated section. However, the important parameter to determine the artifact in the cooling section is not the absolute change in aerosol concentration, but the ratio of that to the change of concentration in the heated section, which we call “re-condensation fraction” (RF). For example, if we have $100 \mu\text{g}/\text{m}^3$ re-condensation (or further evaporation) in the cooling section, the impact would not be the same, if the change in aerosol concentration in the heated section in one case was $200 \mu\text{g}/\text{m}^3$ and $1000 \mu\text{g}/\text{m}^3$ in the other. In the first case, the bias is 50%, while in the second it is 10%. RF is not a function of C_{sat} because the large absolute re-condensation / further evaporation in the cooling section for large C_{sat} is accompanied by a large absolute aerosol evaporation in the heated section. This is evident in the expression of the non-dimensional parameter C_n given in section 2.3. C_n fully characterizes the conditions of the simulation results in Figures 6 and 7.

10.

Including α explicitly in τ would mean substituting the Fuchs-Sutugin (F) in τ . This would make the expression complicated with no substantial gain. We believe that interested readers are aware that F is a function of α , and in any case the expression of F is given in the manuscript.

11.

In section 1, we explain that the use of MFR to characterize aerosol volatility (as has been commonly practiced in the literature) is “theoretically unjustifiable” because MFR is an extensive parameter, which is not uniquely related to C_{sat} , an intensive parameter. An infinite range of MFRs can be obtained for the same aerosol. The physical processes of the TD problem only “care” about how much vapor has been added to the gas phase (i.e. ΔC), not how much of the particle mass remains. While it is true that ΔC can be calculated from MFR and C_0 , this does not change the basic fact that ΔC is the key driving variable. For example, which is more volatile: a compound with MFR = 0.5 at $C_0 = 100 \mu\text{g}/\text{m}^3$ or a compound with MFR = 0.8 at $C_0 = 500 \mu\text{g}/\text{m}^3$? To answer the question, one has to calculate ΔC for both cases, being $50 \mu\text{g}/\text{m}^3$ for the first and $100 \mu\text{g}/\text{m}^3$ for the second, and conclude that the second compound is more volatile. It is obviously more practical and more consistent with the physics to report ΔC right away. We further note that MFR has been reported in the literature *without* C_0 , which leaves the erroneous impression that MFR determines C_{sat} .

In this study, we do not plot ΔC vs. temperature because we are not looking at volatility. Rather, we plot $C_g^* \approx \Delta C/\Delta C_{max}$ vs. residence time to investigate equilibration times. C_g^* is a measure of gas phase saturation, and is used to provide a normalized basis to compare compounds of different volatilities. If we are looking at equilibration times of a single compound, as for example in Figure 2, ΔC can be used instead of C_g^* .

In this work, ΔC_{max} values were *not* assumed to be known a priori for the pure compounds (although they can be calculated from previously reported thermodynamic properties), and as a matter of fact, for one of the experiments “there are multiple compounds involved”. ΔC_{max} was obtained experimentally for each test aerosol by increasing the residence time in the TD until ΔC approaches a maximum value. This procedure can be performed to obtain ΔC_{max} for any system, provided that equilibrium can be achieved in the TD.

If equilibrium is not achieved, it is true that neither ΔC nor MFR can provide enough information about the aerosol volatility, if the aerosol size distribution is not known. This does not change the fact that MFR still requires C_0 , and could be highly misleading when interpreting TD results.

5 & 12.

Dr. Cappa makes an important point about the use of TDs to measure thermodynamic properties of ambient aerosols. As pointed out, we mention that ambient aerosols cannot be expected to equilibrate in TDs, however, experimental peculiarities of determination of thermodynamic properties of ambient aerosols using TD measurements is beyond the scope of this paper. This work focuses on the physics of aerosol equilibration with the aim of resolving some confusion that arose recently with regard to the effect of aerosol volatility on the equilibration time. Indeed, our results suggest that the equilibration is significantly easier for higher aerosol concentrations, i.e. favors laboratory conditions. We realize the importance of ambient TD measurements to the community; we point out the impossibility of equilibrating ambient aerosols with current TD measurement techniques to help set the stage for future research and not to assert that “*TD measurements of ambient aerosol are a pointless endeavor*”. We agree that pending developments in the state of the art, the best approach is to interpret ambient TD measurements using kinetic models as done in Cappa and Jimenez (2010), while keeping in mind the substantial uncertainty due to unknown α , as pointed out by those authors. This discussion will be added to the revised manuscript. We are also confident that eventually an experimental method can be developed that will allow studies of ambient aerosol volatility at near-equilibrium conditions.

Response to Ilona Riipinen

Our replies are numbered according to the numbering of Dr. Riipinen's comments.

1.

Dr. Riipinen argues that our conclusion that equilibration time scales in TDs do not depend on thermodynamic properties of the aerosol is “*not proven convincingly enough in the current version of the paper*”. The first issue is related to the derivation of the characteristic evaporation time (τ). Dr. Riipinen writes:

However, in the derivation of these characteristic times one must assume that the particle size does not change upon evaporation. This is, of course, by definition contradictory to the problem that is being addressed: as the particles are evaporating and reaching equilibrium, their size is changing and the mass flux in the end needs to approach zero. One can, of course, still pick a certain moment t (with a certain $d_p(t)$) of the evaporation process to represent the whole process, but it is not clear how this moment should be chosen and whether the volatility of the evaporating species enters the equation through this size dependence.... The authors should thus either demonstrate with numerical simulations that the change in the particle size during evaporation does not significantly affect their conclusion or suggest how to pick the representative particle size from the evaporation process (i.e. which moment of time in the equilibration process to pick to calculate τ) and show that the size-dependence does not introduce a dependence on the volatility of the species.

One goal of performing dimensional analysis is to elucidate the underlying physics of the problem at hand, a particularly useful exercise when there are many variables. The dimensionless parameter need not be constant throughout the problem for it to shed light on how the variables relate. One can use any diameter (e.g. initial, final, average) to calculate tr/τ , but should be consistent when comparing across different experimental conditions. For instance, our conclusion that $tr/\tau > 9$ indicates equilibration is based on the initial diameter, as given in section 2.3 and 4.4. . In fact, the factor 9 corresponds to the case in which C_{sat} is close to C_0 , such that most of the material evaporates, resulting in large particle size changes. I.e. this large factor of 9 accounts for the effect of the changing aerosol size.

The question of “*whether the volatility of the evaporating species enters the equation through this size dependence*” is an interesting one. It enters in one sense only: aerosols that have a higher volatility require a greater net transfer from the particle to the vapor phase in order to bring about equilibrium. In the event that the initial particle concentration, C_0 , is low, i.e. close to the ΔC needed to saturate the vapor phase, then as the aerosol continues to evaporate the sink diameter decreases rapidly and constricts the kinetics. Thus, in a sense, yes in case the initial aerosol particle concentration is low (i.e. similar to ΔC needed for equilibrium), volatility can impact kinetics by reducing the sink diameter. To illustrate, we can imagine two aerosols with the same τ but different volatilities such that the first can achieve equilibrium with little diameter change while the second requires large diameter change to achieve equilibrium. As

the first aerosol approaches equilibrium, τ remains essentially constant and close to its initial minimum value. As the second aerosol approaches equilibrium and the sink diameter drops considerably, there will be a proportional inflation of τ and therefore the equilibration time. So does this invalidate our assertion that equilibration is not affected by thermodynamic properties? No, because the problem remains controlled by strictly kinetic parameters and the aerosol length (i.e. τ), as demonstrated when vapor build up profiles are plotted versus dimensionless equilibration time (t_r/τ). Figures 4 and 5 in the manuscript demonstrate that vapor build-up profiles coincide in t_r/τ space for C_{sat} values varying over an order of magnitude. However, per Dr. Riipinen request we have added an additional figure (Figure 6 in the revised manuscript) that demonstrates vapor built-up profiles for compounds with C_{sat} values varying by three orders of magnitude, as well as added text discussing this to section 4.4. As the calculations show, provided that $C_{sat}/C_0 \ll 1$, the volatility has no effect on equilibration time, neither in absolute time nor in relative time. When $C_{sat}/C_0 \approx 1$, higher volatility will increase absolute time (strictly via its affect on τ , and for no other reason), but not affect dimensionless equilibration time. And for completeness, when $C_{sat}/C_0 > 1$, equilibration is not possible. We stress again that this result is derivative of the kinetics, and that provided that the aerosol concentration is not low relatively to the required change in C_{sat} , volatility has no effect on equilibration time. The problem is always governed by the dimensionless group τ .

We thank Dr. Riipinen for pointing out the work by Wexler and Seinfeld (1990). We believe that this gives confidence in the validity of our approach, and we will gladly add a reference in the revised manuscript.

2.

It is true that we did not measure the vapor concentrations directly, and that they were inferred from change in particle mass. However, this inference is straightforward; since the wall losses are negligible (see our reply to Reviewer #3), it is based on simple mass balance. We explicitly state in section 3 (line 20 p.2941) that we measure the change in mass (ΔC), and then we show in equation 9 how the dimensionless vapor concentration (C_g^*) is calculated. As for the *“uncertainty of not actually knowing exactly what there is in the vapor phase”*, we believe that this is not an issue. The aerosol generation method guarantees that the aerosol entering the TD is comprised of the organic compound(s) and a negligible amount of water. As for how certain we are that *“there are no additional vapor phase losses/saturation”*, we are confident that there are no such losses, given the excellent agreement between experiment and theory. Please refer to reply #2 to Referee #3 for more details. The error bars in the plots are standard deviations of multiple measurements. This will be clarified in the revised manuscript.

3.

As we mentioned in reply #1, we have investigated the effect of varying volatility by an order of magnitude on the equilibration parameter t_r/τ in section 4.4. Discussion on this issue is added to the revised manuscript.

4.

We agree that information on the evolution of the aerosol particle size is lacking in the current version of the paper. Since the measurements are performed with polydisperse aerosols, it will not be useful to plot the evolution of particle size, but we have added ΔC values measured at different residence times to Figure 2 in the revised manuscript so that it will be easier for researchers performing TD – SMPS experiments to relate our findings to their experimental results, as Dr. Riipinen rightly points out.

Although particle sizes and number concentrations are the variables measured in TD experiments, it is physically unjustified and misleading to define equilibration in terms of particle size. As we describe in the manuscript, and as Dr. Riipinen acknowledges in her comment, equilibration is defined in terms of the saturation ratio (SR) of the gas phase, which is the ratio of vapor concentration to the maximum vapor concentration that air can hold at a certain temperature ($SR = C_g / C_{sat}$). The problem with using particle size a metric for equilibration is that a certain change in particle size corresponds to different %SR depending on aerosol volatility. This was clearly illustrated via the thought experiment in section 4.3. SR can be easily employed as a metric for equilibration in models. For experiments, SR can also be easily calculated from measured quantities using equation 9. Note that $SR = C_g^*$ in the thermally steady part of the TD. We will add this discussion to section 4.3 of the revised manuscript.

Minor comments:

1. We have added a table listing the thermodynamic properties of the test compounds. Conducting sensitivity calculations for the variation of reported thermodynamic values is rather meaningless, as our paper shows: the absolute vapor pressures do not affect equilibration times.
2. We have added more detailed information to Figure captions. The experimental matrix is given in Table 1.

Response to Referee #3

The essence of this reviewer's criticism is that our analysis is fundamentally flawed, because we assign a zero-flux boundary condition for the volatilized material in the heated section of the TD. The reviewer presents an order-of-magnitude analysis of a potential effect the walls could have on the behavior of the system via formation of a molecular monolayer on the walls of the heated section. As the argument goes, the heated TD wall should not be considered as a zero flux boundary, but rather, due to its large surface area, should be considered as a perfect scavenger of the species evaporating from the aerosol to the degree that it renders the gas phase entirely free of aerosol vapors: "*there ain't any molecules in the gas phase*". The reviewer concludes that as a result, the change in aerosol mass as it flows through the TD is not driven by equilibration between the gas and particle phases but rather a continuous stripping process from particle to wall, at a rate controlled by wall adsorption. If the reviewer were correct, this would certainly invalidate our study (and virtually every other TD study for that matter).

The reviewer's reasoning, however, flies in the face of elementary mass transfer and equilibrium thermodynamics theory, but we will simply point to two empirical facts to answer the reviewer's main criticism. The first is that the aerosol mass does not measurably change as the aerosol flows through an unheated TD. If the reviewer's claims were accurate, then aerosol mass would be efficiently stripped regardless whether the TD is heated or not. The second empirical fact is that when the TD is heated (i.e. turned "on"), the entering aerosol initially evaporates and then, in a manner well-predicted by the zero-flux boundary assumption, which the reviewer finds objectionable, the mass change rate approaches zero. If the reviewer were correct, the aerosol would continue to evaporate for the entire length of the TD, and the theory and measurements would not agree. Therefore the evidence demanded by the reviewer is already found in figures 2 and 4 of the manuscript; we are surprised that the reviewer did not, apparently, look at them.

In short, the review appears to be grossly misguided. As will be shown in the detailed replies below, it appears to be of exceptionally low quality because the reviewer apparently did not study the experimental method described in the paper and neglected the empirical evidence presented.

Detailed reply

The referee's comments are indicated in italics.

1.

The statement that the equilibration time is not affected by volatility (pg. 2934, line17-18, repeated several times throughout the text) is certainly untenable. The authors are correct that it is not an explicit relation, however, a look at both governing equations for the gas (eq. 2) and particle mass (eq.3) suffices

that the driving force, i.e. the rate of molecular evaporation/condensation depends on the concentration (or partial pressure) differential: the larger the difference, the faster the rate of relaxation rate. Equations (2) and (3) are linear differential equations whose solution involve exponential terms, and for formal reasons it may help to explicitly note the temporal dependence of T and C_g in terms of $T(t)$ and $C_g(t)$ in the equations. I therefore believe that the discussion whether or not the equilibration time, dimensionless or not, involves $C_{sat}(T)$ or not, rather misplaced. The correct answer probably is that the e-folding time for the relaxation process only depends on the kinetic constants and not on the amount of material to be evaporated, in agreement with the relaxation formalism alluded to above: large changes in C_{sat} lead to a rapid rate of relaxation, small changes in C_{sat} to a low rate, both processes being controlled by the same e-folding time.

It is rather hard to make sense of this comment: the reviewer starts with “the statement that the equilibration time is not affected by volatility... is certainly untenable” and ends with “large changes in C_{sat} lead to a rapid rate of relaxation, small changes in C_{sat} to a low rate, both processes being controlled by the same e-folding time”. Is the e-folding time not one of the measures of equilibration time?! The referee also seems to confuse absolute gas phase concentration (C_g) and dimensionless gas phase concentration (C_g^*). Equilibration in the TD is not defined in terms of C_g , but in terms of C_g^* . For example, if in a certain experiment $C_g = 20 \mu\text{g}/\text{m}^3$, the system would be far from equilibrium, if C_{sat} is $100 \mu\text{g}/\text{m}^3$, but it would be nearly equilibrated if C_{sat} is $22 \mu\text{g}/\text{m}^3$. It is true that C_g is a function of the concentration differential as evident in equation 2, but C_g^* is NOT as shown in equation (5). This is clearly presented in section 2.2, which the referee has apparently not read. Interestingly, the Referee gives the argument that “the e-folding time for the relaxation process only depends on the kinetic constants and not on the amount of material to be evaporated”, which is exactly what we present in section 2.2, and contradicts his/her statement that “The statement that the equilibration time is not affected by volatility (pg. 2934, line17-18, repeated several times throughout the text) is certainly untenable” since volatility dictates “the amount of material to be evaporated”.

2.

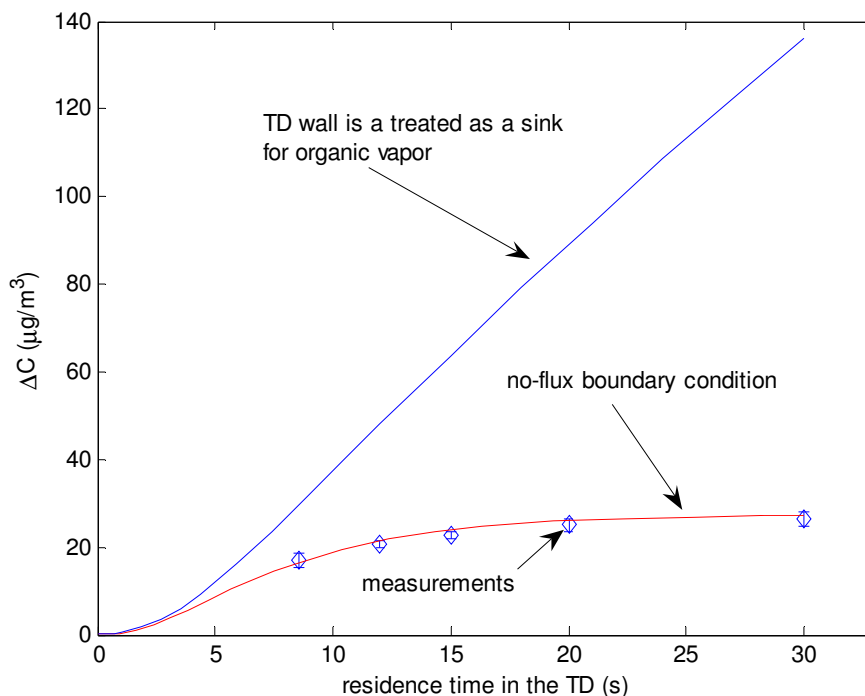
I now make the claim that what the authors are selling as “equilibrium” in their present study is in fact a steady-state and not a true equilibrium. The process they observe is completely dominated by wall-loss of dicarboxylic acid and the associated wall-conditioning by virtue of the small changes of mass involved. Taking a typical value of $300 \mu\text{g}/\text{m}^3$ mass concentration (Table 1) one would transfer a total of 90 ng of aerosol mass into the total gas volume of 314 cm^3 of the TD if evaporated completely. At a typical molecular mass of 100 amu this would amount to 5.4×10^{14} molecule/ cm^2 which corresponds to just about one formal molecular monolayer on a single cm^2 of wall area. However, the total internal wall area of the TD is roughly 800 cm^2 which means that on average one would adsorb 0.1% of a monolayer on average upon complete evaporation of the aerosol. What is the driving force for the wall adsorption process? At a representative ultrafine aerosol diameter of 65 nm and a loading of $5 \times 10^{11} / \text{m}^3$ (Table 1) we have a total external surface of the aerosol of $1.7 \times 10^{-3} \text{ cm}^2$ in comparison with 800 cm^2 on the internal walls of the flow

tube. This represents an area ratio of 2×10^{-6} aerosol/internal wall. In other words, it is a futile attempt to try to establish gas phase equilibration times without observing and understanding the gas phase including the gas-wall interaction. The wall is a huge sink for the aerosol mass and therefore leads to extreme losses of the aerosol mass that are found on the wall, and not in the gas phase. This mass transport towards the walls during typical gas residence times of tens of seconds is masquerading as an "equilibrium constant" that leads to anomalously large vapour saturation values C_{sat} . By the same token, no re-condensation occurs onto the partially evaporated aerosol in the active charcoal filter because there ain't any molecules in the gas phase. I therefore do not recommend publication of this work in AMTD until such time when the authors will have convincingly demonstrated that they indeed reach equilibrium inside their TD.

As we have pointed out in the introduction to our reply to this reviewer, the criticism presented here contradicts the empirical evidence presented in the manuscript. There are several factors, such as the high temperature of the walls, which can prevent formation of such a monolayer. Even if the layer would form, the time to establish it according to the reviewer's own calculations is significantly shorter than the duration of a single experiment, not to mention multiple consecutive measurements. If the wall effect were as strong as the reviewer thinks it is, one would expect a reduction in wall losses with time, as the mono-layer establishes itself on the walls. Yet, no such behavior was observed in our experiments, nor was it apparently observed in experiments by other research groups that use similar methods.

What is more important, the evidence presented in our paper clearly shows that there is no appreciable effect of the walls in the heated section. Figure 2 and Figure 4 in our manuscript clearly show that the aerosol particles cease to evaporate after a certain residence time, which is a clear demonstration that equilibrium is indeed reached in the TD. This is the evidence the reviewer demands; it is already in the paper.

The statement by the reviewer that what we observe can be explained by a steady-state process is, to use the reviewer's own words, "raw nonsense". If the walls were acting as a sink, the change in aerosol concentration in the heated section of the TD would keep on increasing with the residence time and would never approach a plateau. This is obvious from a mathematical point of view or if one takes time to observe Figure 7 in our manuscript. Figure 7 shows what happens in an activated carbon denuder, which is basically a tube, which walls act as a sink, i.e. the same system as the reviewer imagines the heated section of thermodenuders to be. In case there are difficulties in translating negative re-condensation fractions shown in Figure 7, below is a figure showing the effect of wall losses in terms of changes in aerosol concentration. Note the linear increase with time. The initial non-linearity is due to the thermal transient period. Note also the agreement between the observations and the model output, if the no-flux boundary condition is used. What other evidence does the reviewer need?



Experimental and simulated change in aerosol particle mass in the TD.

The argument that our values disagree with those reported by Cappa et al. (2007) and Booth et al. (2009) is highly misleading and is actually based on cherry-picking the data for comparison, as we show in our reply #9 below.

3.

I would like to comment on a few statements by the authors for their own benefit:

I believe that the empirical Fuchs-Sutugin expression can be replaced by the accommodation coefficient α or the uptake coefficient γ in equations (2) and (3). At atmospheric pressure the mean free path λ is approximately 150 nm which leads to a Knudsen number $Kn = 5$ for aerosol particles of 60 nm diameter. This is in the free molecular flow regime owing to the smallness of the aerosol particles considered.

We agree that this could be used as an approximation for dicarboxylic acids. However, our analysis is not limited to those compounds, though we do use them for demonstrating our point, nor is it limited to the particle size of 60 nm. Since the analysis is applicable to any molecular size and any particle size, we do not see any compelling reason to limit our analysis to the free-molecular regime. The referee, however, is welcome to use this approximation for his or her own benefit.

4.

Pg. 2944, line 16-18: I do not know of a "Maxwell equation" that predicts a faster rate of evaporation for an aerosol having a larger value of C_{sat} . Evaporation/condensation kinetics and thermodynamics are independent in first order.

"Maxwell equation" is equation 3 in the paper (see, for example, Fuchs, "Evaporation and Droplet Growth in gaseous medium", Pergamon Press, 1959; Hidy and Brock, The Dynamics of Aero-Colloidal Systems, Pergamon Press, 1970). It is evident that the evaporation rate (i.e. dm/dt) is indeed FASTER for larger C_{sat} , which is a fact we are sorry the referee is not aware of. And, of course, the Maxwell equation describes a kinetic phenomenon, not a thermodynamic one. We tried to find a statement that disputes this, but could not find any on page 2944, line 16-18, nor anywhere else in our manuscript.

5.

Pg. 2944, line 18-22: The partial pressure is independent of the mole fraction as long as there is enough mass to support a partial pressure throughout the vessel. The picked statement is raw nonsense: the partial pressure is an intensive thermodynamic property independent of the quantity (mass).

In the text the reviewer is referring to we are talking about mixtures in aerosol particles, in which case the first sentence given by the reviewer here is, indeed, nonsensical. However, it is not clear where this sentence is coming from, certainly not from our manuscript. In a mixture (which forms an ideal solution, as it is common to assume), the equilibrium partial pressure of a component i in the gas phase is given by Raoult's law as $P_i = x_i P_{sat,i}$, where x_i is the mole fraction. This is simply the statement that we make. We trust that the referee is familiar with Raoult's law.

6.

Pg. 2943, line 23-24: I take exception to this statement: the mass accommodation coefficient α most sensitively controls the return to equilibrium when the slope is steepest (Figs. 2-4), that is at the beginning (short reaction times) and when the system is farthest from equilibrium. Once equilibrium is reached the system is "dead" from a kinetics point of view and completely insensitive to the choice of α .

This comment is quite confusing. On lines 20-21, in the beginning of the very sentence the reviewer is referring to, we say: "When TD measurements are performed at **non-equilibrium conditions** ... the results strongly depend on α ". What part of "non-equilibrium conditions" is objectionable? In fact, the referee essentially re-states our section 4.2, and uses it as a statement of disagreement with the point we make in section 4.2! This comment is perfectly in line with our analysis that the value of α affects the results if the measurements are done at non-equilibrium, but has no effect if the measurements are done at equilibrium. This is exactly where our method (the IVM) has an advantage over the non-equilibrium methods, such as the TDMA, TPD-MS and KEMS, because we strive to achieve equilibrium in our system, while the non-equilibrium methods all require an assumption about the value of α , which is generally unknown.

7.

Why did you exclude the mass transfer to the walls? (Pg. 2939, line 1)

See reply to comment #2.

8.

I fail to see the physical reason why the “total aerosol length” presented on pg. 2939, line 23, controls the equilibration time? The authors should try harder to come up with an intuitive explanation.

We simply substituted the Maxwell equation (equation 2) in the gas phase concentration equation (equation 3) and performed dimensional analysis to obtain equation (5). If the referee can see a physical reason for why dm/dt and dC_g/dt depend on the parameters on the right hand side in equations 2 and 3 (including N and d), he/she should find no problem seeing the dependence of equilibration time on the aerosol length ($N.d$). If equations 2 and 3 are not intuitive for the referee, he/she should refer to fundamental texts on aerosol dynamics and mass transfer.

9.

Concerning the differences in C_{sat} between adipic and pimelic acid: Cappa() obtains only a factor of 0.5 higher C_{sat} of pimelic re adipic acid. Is the factor of three an artefact of the chosen method? By now several groups have worked on the saturation vapour pressure of the lower series of dicarboxylic acids and have reported consistent results (see Both et al. cited above for a recent graph collecting the lower series of dicarboxylic acids). It therefore is incumbent on the authors to either come up with similar numbers or accurate explanations why they don't.

As indicated in the manuscript, the factor of 3 difference in C_{sat} between pimelic acid and adipic acid is at 40 °C, not at 25 °C. Using the Clausius-Clapeyron equation and results from Cappa et al. (2007), one obtains a factor of TWO (NOT 0.5) difference in $C_{sat}(40\text{ C})$ between pimelic acid and adipic acid. Using data from Bilde et al. (2003), one gets a factor of FIVE difference.

The referee is remarkably selective in the choice of studies and compounds to make the claim that “By now several groups have worked on the saturation vapour pressure of the lower series of dicarboxylic acids and have reported consistent results”. This claim is utterly wrong. Saturation pressure values for dicarboxylic acids have been measured using different techniques. The discrepancies in the reported results are within an order of magnitude, sometimes more. Taking the study the reviewer refers to (Booth et al., 2009) as an example, it is true that there is agreement between $P_{sat,298K}$ of adipic acid between Booth et al. (2009) and Cappa et al. (2007), however, the values obtained for succinic acid are an ORDER OF MAGNITUDE different. If this is what the reviewer calls “consistent results”, one just has to wonder why does he/she find a factor of two difference so objectionable. Even more remarkable is the fact that the value of $P_{sat,298K}$ of succinic acid reported in Booth et al. (2009) is closer to our value reported in Saleh et

al. (2009) than to that reported in Cappa et al. (2007). Other studies have also reported results for $P_{sat,298K}$ of dicarboxylic acids which are consistent with our findings (same order of magnitude), e.g. Tao and McMurry (1989), Bilde et al. (2003), Chattopadhyay and Ziemann (2005). It would have been not just incumbent but prudent for the reviewer to study the literature and to be objective in its analysis.

Measuring thermodynamic properties of low vapor pressure semi-volatile organic compounds is a challenging and open research field; it is only natural for there to be discrepancies. For potential reasons / explanations on why this is the case, the referee is encouraged to refer to the discussion in Cappa et al. (2007) and Saleh et al. (2008 & 2009).

10.

Finally, I do not think that more numerical modelling recommended by the other anonymous referee will be of any help in this case because the authors use a model which lacks the most important elementary step in the reaction scheme. More modelling will only lead to more results that are completely besides the point.

This comment indicates that the referee is apparently out of touch with the current thermodenuder research or has some inexplicable issues solely with our research group. Our paper is not just “this case”; the assumption of no flux at the wall, whether explicit or implicit, is universal in the recent papers discussing thermodenuder results (Wehner et al., JAS 2002; Offenberg et al., GRL 2006; An et al., JAS 2007; Faulhaber et al., AMT 2009; Grieshop et al., EST 2009; Huffman et al., ACP 2009 and EST 2009; Epstein et al. EST 2009; Cappa AMT 2010; Cappa and Jimenez, ACP 2010; Riipinen et al., AtmEnv 2010; to name a few in addition to our own papers and some modeling studies that use the results of TD measurements) and we have demonstrated that this assumption yields highly compelling agreement between theory and experiment. It is somewhat ironic that the referee refers to a comment by Ilona Riipinen, who recently published a paper on the same subject as the current manuscript and in which the same assumption is made.

Still, even on its own merit, this statement by the referee once again does not make any sense. If the walls are not a problem and if the residence time is sufficient to achieve equilibrium, there is no need for modeling, because the calculations are very simple. On the other hand, if the walls were significantly influencing the system, the system would be intrinsically dynamic and the only way to interpret the results would be through modeling.

For the referee’s information, the current paper does not deal with the Integrated Volume Method (IVM), the method the referee apparently does not believe, judging by the groundless statements that the IVM does not agree with the (not so) “consistent” results obtained with other methods (see the preceding reply). The IVM has been described in our previous papers, in which it was compared to the other methods and any discrepancies were thoroughly discussed. The current paper, as those by Riipinen et al., 2010 and Cappa 2010, deals with the factors that are most important in interpreting thermodenuder results and whether or not compounds of different volatility would exhibit different equilibration times. The papers by Riipinen and Cappa used models to infer the effect of different parameters. We believe that due to the

relatively large number of input parameters it is quite easy to make misattributions when interpreting the model results. This is why we presented both the theoretical and experimental arguments in addition to the modeling results. It should be also noted that the current models differ in how they are formulated and what processes are included, which could also lead to different conclusions when modeling the same system. For example, the evaporation kinetics in our model is represented in the same way as other models in the literature (e.g. Cappa, 2010; Riipinen et al. 2010, Faulhaber et al., 2009, Saleh and Shihadeh, 2007; Khlystov et al., 2009). Mass transport, on the other hand, has been treated differently in different models. For example, Cappa et al. (2010) and Khlystov et al. (2009) adopted a fully developed laminar flow approach, while Saleh and Shihadeh (2007) adopted a plug flow approach with heat/mass transfer to the TD walls based on average Nusselt/Sherwood number correlations. Vapor concentration profiles predicted by the Saleh and Shihadeh's (2007) plug flow model (which was used in this study) were found to agree with the more detailed Khlystov et al. (2009) model as indicated in section 2.1 (line 18 p. 2938). Also, the model used in this work was validated experimentally using saline aerosols as described in Saleh and Shihadeh (2007). Finally, the fact that model interpretation of the measurements in this study led to α values in very good agreement with the values obtained previously in Saleh et al. (2009) using a different experimental approach (TDMA) increases our confidence in the validity of the model. Still, more modeling studies of the importance of different processes in thermodenuders could further our understanding of and potentially help improve the experimental method itself.

Response to Michel Rossi

We would like to thank Dr. Rossi for the insight on thermodynamic properties of carboxylic acids. Also, his assertion that “*thermodynamics and kinetics are independent of each other*” supports our theoretical and experimental findings.