This paper studies evaporation and condensation behavior of organic aerosol inside thermodenuders. The study consists of experiments and model calculations on the evaporation timescales of dicarboxylic acids. The authors also present model calculations on the possible re-condensationsation in the cooling section of common thermodenuder designs. The authors conclude that equilibration timescales in thermodenuders do not depend on the saturation vapor pressures of the evaporating species, and that at least in the systems they studied the re-condensation in the cooling section was negligible. Instead, if an activated carbon coating was assumed to be used in the simulations, evaporation of the aerosol in the cooling section was predicted at some conditions. The authors also suggest that the absolute change in the mass concentrations of the studied species is a better measure of evaporation than the commonly used mass fraction remaining (MFR). This paper presents an interesting addition to the discussion of evaporation behavior inside thermodenuders. I have, however, a few concerns that the authors should address before this manuscript can be published in AMT.

Major comments:

My main concern is related to the conclusion that the equilibration timescales in the TDs do not depend on the volatility of the evaporating species. I am not saying that this conclusion is wrong, but I think it not proven convincingly enough in the current version of the paper. The authors base the conclusion on 1) a non-dimensional parameter that does not appear to depend on the saturation vapor pressures of the species 2) set of experiments that have been conducted with dicarboxylic acids and their mixtures. I think additional work is needed to prove the conclusion, and a lot of my following comments are related to this issue. This conclusion seems to be to a large extent a matter of definition, and I would thus suggest softening the conclusion a little for the reasons given below.

1. The authors define, based on a non-dimensionalized mass flux to the vapor phase, a characteristic time scale of evaporation in the TD as (see the discussion paper for the definition of the symbols)

[1]

$$\tau = \frac{1}{2\pi N d_{p,i} DF(Kn, \alpha)}$$

This equation is very similar to the equation for equilibration timescale already presented by Wexler and Seinfeld (1990) and referred to later by Seinfeld and Pandis (1998) and Riipinen et al. (2010)

[2]

$$\tau' = \frac{1}{2\pi N d_p DF(Kn, \alpha)}$$

that has been obtained by defining the non-dimensional variables as $C^* = C_g/C_{eq}$, $t^* = t/t_{eq}$, where the subscript eq refers to the equilibrium conditions (where the time derivative of C^*

is 0 – i.e. there is no net transport between the phases – this being the fundamental definition of phase equilibrium). As pointed out by the authors, these equations do not explicitly depend on the volatility of the evaporating species. 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. In our recent paper (Riipinen et al., 2010) we compared the predictions of Eq. [2], as determined using the median size over the full evaporation (from initial size to equilibrium size), to purely numerical predictions and found a fairly good agreement – the Eq. [2] providing an upper limit to the equilibration time scales as compared with our looser definitions of equilibrium (based on the particle size). It is also notable that the transition regime correction F depends on particle size through the Knudsen number – and not only on the mass accommodation coefficient, as pointed out by the authors. 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. This should be rather easy to do by conducting numerical simulations of evaporation of compounds with different volatilities at different conditions (but keeping N and d_{p0} fixed), investigating the behavior of $\tau \cdot d^*$ and comparing it to the magnitude of the other factors in the equation, and thus study the goodness of the assumption that it does not change with varying volatilities and realistic conditions. The authors should also add reference to the work by Wexler and Seinfeld (1990).

As a minor note – I also think that the formulation of Wexler and Seinfeld (1991) is a more reasonable choice for the non-dimensional parameters, as the characteristic time in the limit of equilibration is easy to derive mathematically by letting C^* and t^*approach unity. In this kind of treatment one ends up with the simple equation for the non-dimensional vapor concentration
[3]

$$C^*(t^*) = 1 - (1 - C_0^*)\exp\left(-ut^*\right)$$

where now $C_0^*$is C^* at time 0, and $u = t_{eq}/\tau'$. This formulation shows elegantly how the non-dimensional gas phase concentration depends on the initial conditions (and, if the aerosol is assumed to be initially in equilibrium, bring in a dependence on the saturation vapor pressure or the vaporization enthalpy as shown by Dr. Cappa in his review) and $u.$ It is notable, however, that this simple equation also holds only if u does not depend on t^*. The apparent dependence on the aerosol volatility reported by Riipinen et al. (2010) might also be related to the fact that if 1) the total aerosol mass concentration is kept constant and only the volatility of the aerosol constituents is varied and 2) initial equilibrium is assumed,

by varying the volatility one actually varies the total (vapor + aerosol) concentration of the evaporating species in the system and thus the final equilibrium predictions. Could the authors could comment on this?

2. In Figs. 2-5 the authors refer to "measured vapor build up profiles". However, if I understand correctly, there is no direct measurement of the vapor concentration available, but the "measured" vapor concentration has actually been inferred from measurements of the change in aerosol mass, ΔC. This should be made clear in the paper – or if there is a way to actually measure the vapor concentration, this measurement should be included in the experimental section. Also, the uncertainty of not actually knowing exactly what there is in the vapor phase should be addressed (preferably even somehow quantified). How certain are the authors that there are no additional vapor phase losses/saturation during their experiment? How well-defined is the gas phase exactly? Additionally, I did not find explanation of the error bars in Figs. 2-5 (it might be there but I just missed it). What are these error bars based on?

3. To back up their theoretical argument of the independence of the equilibration time of the authors present experimental results on the evaporation of dicarboxylic acids and their mixtures in their thermodenuder system (Fig. 4). They also say that these results "verify the finding that equilibration time scales are neither a function of C_{sat} or mixture complexity". These results are indeed a good piece of evidence to show that the equilibration does not seem to vary too much in the range of volatilities that they are looking at, but I feel that the compounds that the authors are studying still represent a fairly small range of volatilities. It would thus be good if the authors would, in addition to the experiments, present numerical simulations of theoretical compounds whose volatilities vary over orders of magnitude (which is likely to be the case in the atmosphere) and their mixtures to convince the reader that volatility indeed does not paly a role in the vapor build up profiles (keeping the total concentration and size of aerosols fixed in the simulations).

4. On p. 2944 the authors make the important point that the discrepancy in equilibration timescales between this study and the work by Riipinen et al. (2010) is probably due to different definitions of equilibration time: the authors use the non-dimensional characteristic time (Eq. [1]) whereas Riipinen et al. (2010) defined the "equilibrium" based on the reduction in particle diameter. The authors are correct that particle diameter is by no means the fundamental variable defining equilibrium – but rather it would be the particulate/gas phase mass, or, to be even more exact, the mass/molecular flux between the phases. The particle size and number concentration are, however, the variables that are usually measured when interpreting thermodenuder experiments, not the vapor concentrations or mass fluxes. This is what is done in this paper too. As I mentioned earlier, Riipinen et al. (2010) compared the predictions of Eq. [2] to the size-based criterion and found that the predictions of Eq. [2] served as a good upper limit for the equilibration times – if looking from the perspective of reduction in the particle size. Taking this into account, I think it would be informative if the authors would present, besides the non-dimensional vapor build-up profiles, the

evolution of particle size (since that is the measurable quantity) at least in some of Figs. 2-5. This would allow for people using thermodenuders to relate their experimental results (obtained with an SMPS or DMPS) to the results of this paper. I think that the connection of the results (or the choice of equilibration criterion) to actual measurements also deserves some additional discussion. Generally, I agree with the authors that the change in aerosol mass, ΔC, is a better measure for the evaporation in TDs instead of the commonly-used mass fraction remaining – I think that this suggestion is an important contribution of this paper to the scientific community.

Minor comments:

1. The thermodynamic properties of dicarboxylic acids used in the calculations should be listed. Also, the literature values of these properties show some variation. I think it would be good if the authors would conduct some sensitivity simulations with property values that have not been inferred from their own experiments, and point out the uncertainty in the simulations that would be caused by variation in the literature properties of the acids.

2. I suggest the authors indicate the meanings of the different curves in Figs. 2-5 with a legend rather than in the caption and report the different experimental conditions in a table.

References:

Riipinen et al., Atmos. Environ., 44, 597-607, 2010.

Seinfeld and Pandis, Atmospheric chemistry and physics, 1998.

Wexler and Seinfeld, Atmos. Environ., 24A, 1231-1245, 1990.