

Referee Report on manuscript amt-2010-79 „On transport phenomena and equilibration time scales in thermodenuders“ by R. Saleh, A. Shihadeh and A. Khlystov submitted to Atmospheric Measurement Techniques Discussions”

At first sight this paper looks sound, both from a formal (theoretical) as well as from an experimental point of view. The authors make a few pertinent remarks and observations dealing with the dimensionless treatment of the relaxation kinetics to chemical equilibrium between the gas- and condensed phase in the form of aerosols inside a thermodenuder (TD). Upon entering the hot section of the TD a different evaporation/condensation equilibrium constant is imposed on the system, and the evaporation/condensation kinetics leads to relaxation of the multiphase system towards the new equilibrium. The formalism, i.e. the approach to the new equilibrium, has been introduced and applied by M. Eigen in the nineteenfifties in Göttingen for which he was later rewarded the Nobel prize in chemistry (1967). In addition, the discrepancy between ΔC (change of absolute mass fraction of aerosol) and mass fraction remaining (relative metric) is rightly pointed out. Why not follow Riipinen's suggestion in the accompanying comment of plotting both so that the reader may convince himself of the relative advantages of both (equivalent) representations of the same facts?

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.

However, the authors are completely missing the point in relation to the accuracy of the physical chemical model dealing with low volatility dicarboxylic acids. The chosen experimental method as well as the associated model are completely unsuitable for the problem at hand because the change in aerosol mass via measurement of the change in the mobility diameter of the aerosol particles is too coarse a metric for the measurement/calculation of the equilibration time of such low vapour pressure compounds. From Saleh et al. (Aerosol Sci. Technol. 44, 302, 2010) and Cappa et al. (J. Phys. Chem.

A 111, 3099, 2007) I gather that the saturation vapour pressure at 298K of azelaic (C9-dicarboxylic) and adipic (C6-dicarboxylic) acids are different by three decades and a factor of 20, respectively, with the method used by Saleh et al. yielding consistently higher values. 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 it stands the authors are presenting a measurement artefact with an interpretation of their data as an equilibrium without knowing the composition of the gas phase. I also would advise them to seek a simpler chemical system for the validation of their experimental technique involving molecules whose surface residence times (= inverse of the first-order desorption rate constant $1/k_d$) is significantly smaller than for dicarboxylic acids which are a hard nut to crack owing to their low values in C_{sat} at ambient temperatures (see for example Booth et al., Atmos. Meas. Tech., 2, 355–361, 2009). The winning strategy will be the simultaneous observation of the gas- and the condensed phase, primarily because proof of gas-phase equilibrium (perturbed by wall reactions) has to be checked against the mass balance.

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.

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