

Review of “On Transport Phenomena and Equilibration Time Scales in Thermodenuders” by Saleh et al. (Atmos. Meas. Tech. Discuss., 3, 2931–2960, 2010)

The paper by Saleh et al. is an interesting contribution to the ongoing discussion of how to best interpret aerosol volatility measurements made using thermodenuders. The authors add some important new insights towards the interpretation of TD measurements, in particular with respect to understanding how well equilibrium is/is not obtained for a given configuration/aerosol system. In my opinion, the most important finding from this study is that, for typical TD configurations (and likely for any realistic TD configuration), equilibrium will not be obtained when measurements are made for ambient aerosol. For laboratory systems it is possible to design experiments wherein equilibrium can be achieved and therefore used in the measurement interpretation, but for ambient measurements it is not appropriate to interpret the observations assuming equilibrium had been achieved in the TD.

I believe that this paper is publishable after the authors address my comments below. I’ve tried to use the same nomenclature as Saleh et al. throughout.

1. The non-dimensionalized analysis presented by Saleh et al. is a useful contribution towards how to think about the evolution of the particle and gas phase in a thermodenuder. They make the important observation that the non-dimensionalized gas-phase concentration ( $C_g^* = C_g/C_{sat}$ ) can be characterized by a dimensionless parameter,  $t/\tau$ , that does not depend on the thermodynamic properties of the aerosol, in contrast to the conflicting conclusions of Cappa (2010) and Riipinen (2009). However,  $dC_g^*/dt^*$  does depend on  $(K-C_g^*)$  as well (see their Equation 5). The calculation of  $dC_g^*/dt^*$  therefore depends on  $C_{sat}$  which is a temperature dependent property. Under the assumption that the system starts in equilibrium at ambient temperature then  $C_g = C_{sat,0}$ , where the subscript zero indicates the initial state. Then, assuming the temperature dependence of  $C_{sat}$  can be described using Clausius-Clapeyron where:

$$C_{sat} = C_{sat,0} \left( \frac{T_{ref}}{T_d} \right) \exp \left( \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T_d} - \frac{1}{T_{ref}} \right) \right)$$

where  $T_{ref}$  is the initial temperature,  $T_d$  is the TD temperature and  $\Delta H_{vap}$  is the enthalpy of vaporization, the  $dC_g^*/dt^*$  relationship can be rewritten as

$$\frac{dC_g^*}{dt^*} \propto \left[ K - \frac{C_g}{C_{sat}} \right] = \left[ K - \frac{C_{sat,0}}{C_{sat}} \right] = \left[ K - \frac{C_{sat,0}}{C_{sat,0} \left( \frac{T_{ref}}{T_d} \right) \exp \left( \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T_d} - \frac{1}{T_{ref}} \right) \right)} \right];$$

$$\frac{dC_g^*}{dt^*} = \left[ K - \frac{T_d}{T_{ref}} \left[ \exp \left( \frac{-\Delta H_{vap}}{R} \left( \frac{1}{T_d} - \frac{1}{T_{ref}} \right) \right) \right]^{-1} \right]$$

Thus, we see that in fact the variation in the dimensionless gas-concentration does depend on the thermodynamic properties of the aerosol, albeit not in the manner previously alluded to in Cappa (2010). Specifically,  $dC_g^*/dt^*$  depends on the enthalpy of vaporization, as this characterizes how rapidly the saturation concentration will change from the value at room temperature. In fact, if we make the reasonable assumption that lower vapor pressure compounds have higher enthalpies of vaporization, then  $dC_g^*/dt^*$  will be larger for lower  $C_{sat,ref}$  compounds at a given TD temperature, indicating that lower  $C_{sat,ref}$  compounds may equilibrate somewhat faster than higher  $C_{sat,ref}$  compounds (where  $C_{sat,ref}$  is the saturation vapor pressure at the reference, not the elevated, temperature). However, this is only a result of compounds having different enthalpies of vaporization and not different  $C_{sat,ref}$  values. I would suggest that the authors consider this extension of their presentation in the revised manuscript. The sentence beginning on line 19, page 2939 should be revised accordingly.

2. The authors should include the thermodynamic parameters for the diacids considered in this study in Table 1 or in the text.

3. In equation 9 the last equals sign (=) should be replaced with an approximately equals sign ( $\approx$ ) to indicate more clearly that they have made an assumption that  $\Delta C \gg C_{sat}(25^\circ\text{C})$ . It would be useful if they would explicitly make this statement, rather than just stating in words that  $C_{sat}(40^\circ\text{C}) \gg C_{sat}(25^\circ\text{C})$ . Also, this assumption should be justified more completely. At what level do they assume that they can neglect  $C_{sat}(25^\circ\text{C})$ ? For example, if  $\Delta H_{vap} = 70$  kJ/mol, then  $C_{sat}(40^\circ\text{C})/C_{sat}(25^\circ\text{C}) = 3.7$  and  $\Delta C/C_{sat}(25^\circ\text{C}) = 2.7$ . This hardly seems a large enough difference to neglect the  $C_{sat}(25^\circ\text{C})$  term. This is especially true when one considers this equation more fully, which only has the maximum  $\Delta C$  in the denominator; in the numerator the value considered is simply  $\Delta C$ , or the change in aerosol concentration up to that point. At early times or for short residence times (compared to the equilibration time)  $\Delta C$  may not be large compared to  $C_{sat}(25^\circ\text{C})$ . In this study Saleh et al. consider a number of dicarboxylic acids, which all have relatively high  $\Delta H_{vap}$  values, meaning that  $C_{sat}(40^\circ\text{C})/C_{sat}(25^\circ\text{C})$  may be large, for example equal to 9.7 for  $\Delta H_{vap} = 120$  kJ/mol. Since the compounds considered here have “large”  $\Delta H_{vap}$  values they may be better suited to this particular type of analysis than compounds with lower  $\Delta H_{vap}$  values. Can the authors comment on this? Perhaps they could consider this in a general way using, e.g. the semi-empirical  $C_{sat}$   $\Delta H_{vap}$  relationship given by Epstein et al. (2010) as a test?

4. Section 4.1: The authors present an interesting and important result: namely that the equilibration time-scale depends explicitly on the total particle number concentration or, more specifically, particle mass loading for a given particle diameter. Unfortunately, I find the language here to be a bit confusing. They refer to the “total particle length” and mention that the equilibration time is dependent on “particle size distributions.” I think it would be clearer to simply state that, for a given particle diameter, the equilibration time is dependent on the particle number concentration. This seems more appropriate as  $\tau \propto d_p N_{tot}$ , and not only  $N_{tot}$  or  $d_p$  alone (where  $d_p$  is the initial particle diameter and  $N_{tot}$  is the particle number concentration). Also, the authors state that “for size distributions relevant for ambient measurements, equilibration requires residence times much larger than what is available with current TD designs.” I would suggest that a better term to use than “size distributions” would be “particle mass

loadings.” Incidentally, this statement seems to inherently supports the conclusions in Cappa (2010), namely that for interpretation of ambient TD measurements it is important to use a kinetic model.

5. Section 4.2 and 4.1 and 4.4: The authors state that “when  $\alpha$  is unknown, it is critical that TDs are used in a manner such that measurements are made under equilibrium conditions.” However, in the previous section they stated that “for size distributions relevant for ambient measurements, equilibration requires residence times much larger than what is available with current TD designs.” Given that current TD designs will not allow ambient aerosol to reach equilibrium, can the authors provide concrete suggestions on what sort of residence time they believe necessary for making “equilibrium” ambient measurements? This would be of high interest to the community. They could provide necessary residence times assuming  $\alpha = 1, 0.1$  and  $0.01$  and a “typical” ambient size distribution and mass loading. In other words, it would be useful if the authors provided some specific examples in addition to the more general equation. For example, using  $D_{p,in} = 300$  nm,  $N_{tot} = 300$  particles/cm<sup>3</sup>,  $D = 3 \times 10^{-6}$  m<sup>2</sup>/s and  $F = 1$  (which corresponds to a mass loading of  $\sim 4.2$   $\mu\text{g}/\text{m}^3$ , assuming unit density), one calculates  $\tau = 589$  seconds. Thus, to get to  $9\tau$  requires 5310 seconds, or 88 minutes. It seems entirely unreasonable to think that a TD could be built with an 88 minute residence time (assuming my calculations are correct). Can the authors comment on whether they believe TD’s could actually ever be used to make equilibrium measurements for ambient aerosol? Although this is mentioned in the abstract, I would encourage the authors to be more bold and state that TD’s cannot be used to determine equilibrium properties of ambient aerosol.

6. Although I believe that the experiments as presented are of high quality, I have some trouble taking these specific results as solid validation of the theoretical predictions. The reason for my concern lies with the nature of the compounds chosen for testing. The vapor pressures of the two pure diacids chosen only differ by a factor of 3 and the “average” vapor pressure of the diacid mixture is likely to differ by much more. With respect to the mixture, I believe this is the case because 1) the mixture is 1:4:4:1 of succinic, adipic, pimelic and azelaic acid. Thus, 80% of the mixture is adipic and pimelic acid, which have similar properties. And the other 20% is composed of two compounds whose vapor pressures bracket adipic and pimelic acid, with an average vapor pressure approximately only slightly lower than adipic acid. As such, the average mixture properties may not really deviate very strongly from adipic or pimelic acid alone. Was there a reason that the authors did not perform the single component experiments using e.g. succinic and azelaic acid, which have vapor pressures at 25°C that differ by orders of magnitude? This would certainly provide more convincing evidence.

7. Figures: Since many of the figures are in color, the authors should mention the colors in the figure captions in addition to the shapes. Even better would be to include legends in the figures.

8. Figure 5: The authors state that figure 5 is comprised of the data from Figures 2 and 4. However, it is not stated explicitly to which experiments the different symbols correspond. Also, I find the presentation confusing with respect to the symbols/colors used. Presumably, three experiments are for adipic acid, one for pimelic acid and one for the mixture. Three colors are used, but they do not appear to correspond to type of aerosol (e.g. there are two symbol types that are red and two that are green). I would suggest that the authors either use different colors for all symbol types or make experiments with

the same compound (e.g. the adipic acid experiments) the same color but with different symbol types. Regardless, which experiment is which should be indicated in the figure, either in the caption or as a figure legend or both. Also, I would recommend that the y-axis in this figure (and Figures 2 and 3) be labeled not only as  $C_g^*$ , but as " $\Delta C/\Delta C_{\max} \sim C_g^*$ " to remind the reader that  $C_g^*$  was not directly measured, but was inferred from the aerosol size change. More generally, the authors should provide a discussion of how  $\Delta C_{\max}$  was determined for each experiment. For some experiments it could be observed as the  $\Delta C$  at long residence times, but for other experiments, where the system was still far from equilibrium at the longest residence times considered,  $\Delta C_{\max}$  could not be experimentally assessed. In these cases, I assume that  $\Delta C_{\max}$  was determined from theory, using the known properties of the compound (i.e.  $C_{\text{sat}}(25^\circ\text{C})$  and  $\Delta H_{\text{vap}}$ ) as input? This is not clear from my reading of the text.

9. In the case of recondensation, the authors come to the conclusion that, in general, whether one has or doesn't have an AC denuder will only minimally influence the observations. But there may be circumstances where the AC denuder imparts a negative bias to the measurements through continued evaporation of the semi-volatile aerosol. The authors show this explicitly in Figure 7 for some test case. However, no conditions are given for this test case. Unlike the equilibration time in the heated section, I would think that the magnitude of the AC artifact will depend explicitly on the vapor pressure of the compound (for a single component aerosol). This is because the loss rate to the walls varies as  $(C_g - 0)$ . Using their Equation 5 and combining with Equation 2 (assuming  $C_w = 0$ ), one obtains:

$$\frac{dC_g^*}{dt^*} = \frac{t_r}{\tau} (K - C_g^*) + \frac{4t_r}{d_t} h_m (0 - C_g^*).$$

Then, Equation 3 can be re-written as:

$$\frac{dm_p}{dt} \frac{1}{C_{\text{sat}}} = -2\pi d_p DF (K - C_g^*)$$

or, solving the above for  $C_g^*$  and substituting, one finds

$$\frac{dm_p}{dt} = -C_{\text{sat}} 2\pi d_p DF \left[ \frac{\frac{dC_g^*}{dt^*} + K \frac{4t_r}{d_t} h_m}{\frac{t_r}{\tau} + \frac{4t_r}{d_t} h_m} \right]$$

Thus, it appears that  $dm_p/dt$  does depend on the saturation vapor pressure of the compound of interest, and will be higher for compounds with larger vapor pressures.

However, I realize that the substitutions made above may not be completely fair because in the original derivation of  $dC_g^*/dt$  made the assumption of no mass-transfer to the walls. Therefore, if one simply starts from their Equation 2 (and uses a single particle size), then one can show that

$$\frac{dm_p}{dt^*} = -\frac{C_{sat}}{N_i} \left[ \frac{4}{t_r d_t} h_m C_g^* + \frac{dC_g^*}{dt^*} \right],$$

which is very similar to the above equation. In either case, we see that  $dm_p/dt^*$ , which is most important in determining the magnitude of the AC artifact, depends explicitly on  $C_{sat}$ . Therefore, it is important to know more about the specific conditions employed in generating Figure 7.

10. The equilibration parameter: Wouldn't it be better to include  $\alpha$  explicitly in the calculation of  $\tau$ , and therefore of  $t_r/\tau$ ?

11. The authors argue that the parameter  $\Delta C$  is more appropriate to use than mass fraction remaining, as MFR inherently depends on the concurrent aerosol mass loading. However, nowhere do the authors actually plot  $\Delta C$  itself vs. temperature; instead they generally plot  $\Delta C/\Delta C_{max} \sim C_g^*$ , although this is done so as to investigate the timescales associated with the approach to equilibrium. This works fine for known systems, but it is unclear how this can be applied to systems where  $\Delta C_{max}$  is not known a priori or where there are multiple compounds involved. In any case,  $\Delta C$  is related to MFR, since MFR is just equal to  $(C_0 - \Delta C)/C_0$  or  $\Delta C = C_0(1 - \text{MFR})$ . Thus, MFR can easily be converted to  $\Delta C$  and vice versa, assuming that  $C_0$  is known (which it always is, even if it's not always reported in articles). Also, returning to the point that for ambient measurements equilibrium is likely to never be achieved in a TD, a plot of  $\Delta C$  vs. denuder temperature would not necessarily be any more meaningful than MFR. I would suggest that the authors add to the discussion of using  $\Delta C$  to characterize evaporation in a TD with this in mind. This discussion is not meant to suggest that I think that MFR is more meaningful than  $\Delta C$ , only that they are multiple ways to look at the problem, especially when considering ambient measurements. Perhaps a "compromise" position would be to suggest plotting both  $\Delta C$  and  $\Delta C/C_0$  (which normalizes to 1 for the maximum  $\Delta C$ ). This would allow readers to see both the absolute and relative changes in a single graph.

12. Given that equilibrium will not be obtained for ambient aerosol in a TD, do the authors have a suggestion of how to best deal with the fact that the evaporation coefficient for complex organic aerosol is not known a priori? As noted above, the authors suggest that "when  $\alpha$  is unknown, it is critical that TDs are used in a manner such that measurements are made under equilibrium conditions." However, this will never be the case for ambient aerosol. Does this mean that TD measurements of ambient aerosol are a pointless endeavor? I should hope not. I would suggest that the authors address this in section 4.2 by suggesting that in cases where  $\alpha$  is not known and equilibrium cannot be obtained, such that a kinetic model must be used, people default to using  $\alpha = 1$ , and very clearly note that their analysis has been made with this assumption in place. Or, alternatively, people can explore the impacts of using different  $\alpha$  values, as was done in Cappa and Jimenez (2010).

References:

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