**Atmospheric
Measurement
Techniques
Discussions**

Interactive comment on "On transport phenomena and equilibration time scales in thermodenuders" *by* R. Saleh et al.

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Riipinen in her remark 1 rightly points out that the temperature dependence of C*g is controlled by the standard enthalpy change of vaporization (DH0vap) which corresonds to the coefficient for the T-dependence of the concentration or partial pressure change. However, a higher value of DH0vap for longer chain dicarboxylic compounds will be off-set by a larger entropy change because it is the free energy of vaporization that controls the partial or saturation vapor pressure. The statement that lower Csat,ref compounds equlibrate faster than higher Csat,ref is, however, untenable as thermodynamics and kinetics are independent of each other. Two compounds of the same vapor pressure may have significantly, sometimes orders of magnitude different rates of evaporation,

in turn their corresponding condensation (mass accommodation) coefficients must be different by that same factor if their vapor pressures are to be the same.

As a case in point one may look at the monocarboxylic acid series formic (373.9K; 22.69 kJ/Mol), acetic (391.1; 23.69), propionic (414; 32.14) and butanoic acid (436; 40.45) for which thermodynamic data are available (compilation of V. Majer and V. Svoboda, Enthalpies of vaporization of organic compounds, IUPAC Chemical Data Series no. 32, 1985, Blackwell Scientific Publications). The first number in the bracket is the normal boiling point, the second is the enthalpy of vaporization at the boiling point except for the latter two acids where it is for standard conditions (approx. 5-10% difference). The entropoy of vaporization (at boiling, that is non-standard conditions) is given by DSvap = DHvap/Tboil and amounts to 60.7, 60.6, 77.6 and 92.8 J/Mol K. As you may see Trouton's rule of a constant value for "normal" liquids (approx. 88 j/Mol K) does not apply to the acids for known and expected reasons (association in the vapor phase). In essence, the increasing DHvap in the series is offset by an increasing value for DSvap. However, all this has nothing to do with the RATES of evaporation and condensation for which there are very few reliable data, especially for organic molecules. There are values for H2O ice (Delval et al., PCCP 6, 4665, 2004; Pratte et al. JCP A 110, 3042, 2006) because evaporation rates determine the evaporative lifetime of ice particles in the atmosphere. The value of "alpha" (mass accommodation coefficient) given by Saleh et al. for dicarboxylic acids ("alpha" approx. 0.1) seems rather high, but not inconsistent.

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