Atmos. Chem. Phys. Discuss., 13, C322–C324, 2013
www.atmos-chem-phys-discuss.net/13/C322/2013/

**Atmospheric
Chemistry
and Physics
Discussions**

Interactive comment on "Kinetic regimes and limiting cases of gas uptake and heterogeneous reactions in atmospheric aerosols and clouds: a general classification scheme" *by* T. Berkemeier et al.

Anonymous Referee #1

Received and published: 4 March 2013

The manuscript describes a scheme for classifying the different regimes for heterogeneous reactions and gas uptake on aerosol particles. It extends earlier treatments by some of the authors, seeking to establish a rigorous framework for treating the kinetics of aerosol transformation. In many ways the work represents a logical extension of earlier work. Although I find very little that should be specifically questioned in the manuscript (it all largely seems to follow correctly and presents an incremental development of previous work), there are some areas of the manuscript that are particularly impenetrable for the reader. I also feel there are some more broad ranging questions

that the authors should consider in any revised version of the manuscript. Specifically:

- The manuscript is overly long and full of a large number of acronyms. In many places the reader has to work very hard to disentangle the acronyms for the different limiting cases, different fits, and kinetic symbols. In many cases it feels that the authors are trying to say something fairly straightforward but the manuscript is certainly not written in a straightforward way. This will reduce its impact. I recommend the authors consider reducing the discussion in some places, moving some of the more detailed arguments into more appendices and spelling out the meaning of some of the more significant acronyms throughout, rather than using a complex array of acronyms. It would be helpful to just use the name of the limiting case: even though this may make some sentences longer, it will make them easier to understand.

- The significance of the numbers that come out of the fitting to the experimental data for oleic acid is not clear (Table 6). Some of the numbers retrieved are highly variable from measurement to measurement, fit to fit (for example, the value of the accommodation coefficient of ozone on oleic acid surface). The measurements represent a variety of experimental techniques, some resolving size changes and some changes in chemical composition. These are clearly not the same thing and it raises the question of how they can be compared. Further, it is my understanding from the discussion early on in the paper that the model that is being used does not even include the gas-particle partitioning of volatile and semi-volatile products (Page 1003: "As the KM-SUB model does not explicitly treat the products of this reaction, limiting cases were assigned at the point where 50% of the initial reactant Y was consumed using the numerical criteria"). Clearly this leads to ambiguity in how the size and compositional data can be compared. It could also have a significant consequence for the course of secondary chemistry and it is apparent that this is not included in the model with the speciation apparently limited to generic X and Y, ozone and oleic acid.

- Although the authors do go to great length to address the sensitivity of the model fitting to the various model parameters, I am still left wondering how unique the fits are, particularly when the measurements at only a handful of points are compared to simulations in which the sensitivities to many parameters are explored. On pages 1017, the authors state: “This example demonstrates the breadth of possible behaviors for cases that do not fall into a distinct limiting case but rather exhibit regime behavior.” This indeed seems to be the main conclusion but is this a surprise? Maybe I am misunderstanding the method used by the authors to fit the oleic acid but they seem to have exclusively focussed on the sensitivity of fitting the data after 10% of the reaction has occurred (i.e. at one specific point during the reaction). On page 1016 they state: “Sensitivity coefficients are given at 10% reaction course as this will reduce the potential influence of reaction products and avoids the initial, highly transient behaviour which is expected as the surface and first bulk layers come into equilibrium with the gas phase.“ Although their rationale is clear, how is limiting their sensitivity analysis to only one region of time consistent with the recognition that different regimes exist and, presumably, their expectation that the model should be capable of separating out the interplay of different kinetic parameters when different regimes are active?

- It is not clear what conclusions on the oleic acid system are being reached. How do their conclusions about the limiting cases compare with the conclusions reported by the authors of the original papers? A truly unique outworking of the model framework would be if it was used to fit all of the data from all of the measurements made in one global fit. I do not believe the authors have done this – the fits in Table 6 appear to be independent for each experiment.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 983, 2013.