Author comment to anonymous referee #2

Referee comment 1:

This paper presents the conceptual framework and proof-of-concept-type applications of a systematic classification scheme for heterogeneous reactions. The authors defined different regimes based on three quantities: the reaction location (surface versus bulk), the supply of reactive gas (reaction-diffusion limited versus mass-transfer limited), and the "well-mixedness" of the system (well-mixed versus gradient-limited). These quantities can vary independently, hence form a three-dimensional space. Based on this, eight limiting cases were identified. After establishing this conceptual framework, the authors applied it to some idealized test cases and also the oleic acid/ozone system by performing numerical simulations with a detailed multiphase model (KM-SUB).
This work builds nicely on previous work done by several co-authors by effectively using the PRA framework in combination with a state-of-the-art explicit multi-layer model for multiphase processes to explore these processes. I view this paper as a very valuable contribution to the knowledge in this field, since it provides a comprehensive framework of how to think about and categorize heterogeneous processes relevant for atmospheric aerosols and clouds. It fits within the scope of ACP, and I recommend it for publication. However, the challenge with this paper is how to present the content so that it is accessible to a wider audience. The first 4 sections are relatively straightforward to follow, and I appreciate the authors' efforts to define and stick with a consistent notation (consistent also with prior papers). However, in particular the presentation of the simulation results in sections 5 and 6 should be improved before publication. A concern about the practical usefulness of this framework is listed under point 3 below.

Response:

We thank anonymous referee #2 for the review and the very positive evaluation of our manuscript. The explicit and constructive suggestions for improvement are very welcome and will be implemented upon revision. We will especially improve the overall readability of Sects. 5 and 6 in the revised manuscript; detailed responses to the referee's comment follow below.

Referee comment 2:

Specifically, I suggest the following modifications:

1 Use of acronyms: In general it would be helpful to keep the use of acronyms in the text to a minimum. Examples for this are the use of "SR" and "MP" within the text of sections 2.3.2 and 2.3.3. Or, in sentences like the one on page 1006, line 16: "e.g. change in reactive uptake coefficient as a function of rp or [X]g", change this to: ""e.g. change in reactive uptake coefficient as a function of particle radius rp or gas phase concentration [X]g". Small changes like this will help making this manuscript more readable.

Response:

The authors think that the employed acronyms are very useful when talking about the topic and also for easier depiction in figures. However, we agree that the text can be more easily understood if acronyms are used less often. As a solution, we will offer the full name of a previously defined acronym as needed throughout the manuscript. We will write out all acronyms at least once in each section and additionally in a number of other places where this might be helpful. This procedure should improve the readability and still should not crowd the manuscript with repetitions of spelled-out acronyms.

Referee comment 3:

2 Readability of figures: Figures 5 and 6 are way too small, hence hard to read. Is this possibly an artifact of the formatting for the ACPD version? For the revised manuscript, I definitely

recommend to make sure that these figures are large enough. Also enlarge the boxes in Figures 2 and 3 so that the labels can be in a larger font.

Response:

We agree that these figures are difficult to read and will be improved in the revised manuscript. We note that the box sizes in Figs. 2 and 3 have been intentionally chosen small to represent the "extreme behavior" in every quantity, which is needed to classify a system as falling into a limiting case. In the revised figure, the boxes remain small but we have increased the font size of the labels for clarity.

Referee comment 4:

3 Practical usefulness of the classification approach: From the example of the Ziemann data set I conclude that for the same experimental dataset, using two different parameter sets, one can arrive at the assignment of two different regimes. So given that many of the parameters listed in Table 6 are not well constrained at all (for example kBR and kSLR), I wonder how useful this approach is in practice. The authors discuss this somewhat in the conclusions, but this shortcoming should also be clearly stated in the main body of the manuscript.

Response:

The overall scheme provided in this manuscript should be seen as a tool to classify kinetic systems once the basic kinetic parameters of a reaction system according to a specific kinetic model (e.g. KM-SUB, Shiraiwa et al., 2010) are known. We freely admit that some parameters are not well constrained in these fits to experimental data. *The process of fitting a specific depth-resolved model to experimental data is not a part of our classification scheme and has to be seen as an individual step. Furthermore, non-limiting kinetic parameters are in general poorly constrained by fits to experimental data, which is most apparent when fitting to a single data set. The fact that a single data set cannot be assigned to a unique regime does thus not narrow the usability of the classification scheme but rather points to the difficulties of interpreting data sets with limited coverage of parameter space. We are currently working on methods that enable global fitting of numerical models to multiple data sets but see this as a further, autonomous step in method development. Of course, the classification system proposed here will only start to gain practical usability after combination with a reliable fitting procedure that delivers unique, well-constrained fits based on several experimental decays. Since this is an important message for us which doesn't seem to come out clearly enough from the text, we will add a clarifying paragraph to Sect. 6 and thank the referee for his thoughtful suggestion.*

Referee comment 5:

Minor remarks:

- Page 1009, line 2: Shoud read [X]gs read [X]g?
- Page 1010, lines 2-9: Should S(rp) read Sn(rp)? Table 4 uses yet a different variant of notation for the sensitivity coefficients. These are admittedly small details, but for a paper like this consistent notation is key.
- "the oleic-acic–ozone reaction system": hyphen between oleic and acid and en dash between acid and ozone.
- Table 5: Note in the caption that the Cases 1-5 refer to the cases in the original papers.
- Figure 6: Are there error bars available for the Ziemann data and the Lee&Chan data? Also, it seems strange to extend the time axis to 35 s, while there is no data beyond 15 s.
- Page 1015, line 14: Which one is the SB_ regime mentioned here and in Table 6. Shouldn't I expect finding one of the regimes listed in Table 3?

Response:

We thank the referee for catching a lot of small details. Especially the notation for sensitivity coefficients has to be standardized urgently for the revised manuscript. We will apply the suggested changes if not otherwise stated in the list given below.

- *We adopted the spelling of the reaction system from the most recent review paper on the oleic acid – ozone reaction system (Zahardis and Petrucci, 2007) and would like to keep this notation to be consistent with that work.*
- *Error bars for data in Ziemann (2005) and Lee et al. (2007) are not available in their respective original publications.*
- *The cutout of the data in Fig. 6(a) has been chosen to match the respective figures in Pfrang et al. (2010) and Shiraiwa et al. (2010), for comparability and easier recognition, but could be changed easily if the reviewer or editor has a strong opinion that it should be so modified.*
- *Even though Tab. 3 gives an exhaustive list of all possible limiting cases, it does not show all possible kinetic regimes. A kinetic regime is a rather subjective construct that arises from omission of decision steps in the classification scheme and can often be imagined as spatial connection of limiting cases in Fig. 2, including the space that lies between and around them (as described in Sect. 2.2). As an example, the SB^{α} regime mentioned on page 1012 in line 14 is generated by omitting the determination of the reaction location in the first decision step, while decision step 2 and 3 point towards accommodation limitation. It thus contains the limiting cases S^{α} and B^{α}, which would be fairly hard to depict in Tab. 3.*

References:

Lee, A. K. Y. and Chan, C. K.: Single particle Raman spectroscopy for investigating atmospheric heterogeneous reactions of organic aerosols, Atmos. Environ., 41(22), 4611–4621, 2007.

Pfrang, C., Shiraiwa, M. and Pöschl, U.: Coupling aerosol surface and bulk chemistry with a kinetic double layer model (K2-SUB): oxidation of oleic acid by ozone, Atmos. Chem. Phys., 10(10), 4537–4557, 2010.

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