

## Response to the review comments by D. Knopf

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The original comments by D. Knopf are copied in black below, our response is given in *blue italics*.

This manuscript represents the 6th installment of the IUPAC Task Group on Atmospheric Chemical Kinetic Data Evaluation on heterogeneous reactions involving aqueous particles. The uptake coefficients and adsorption parameters for various gas phase species on four aqueous surfaces have been considered including liquid water, deliquesced halide salts, other aqueous electrolytes, and aqueous sulphuric acid. An introduction into the various aspects of uptake kinetics is given to assist in understanding the evaluated parameters for description of the underlying kinetics. For each case the available experimental data is presented and a recommendation of parameters is given. This document represents a very good summary of the literature and an extensive evaluation considering that the authors placed the various experimental data into a unifying framework which made it necessary to reanalyze the laboratory data. This approach will allow parameterization of the heterogeneous kinetics in atmospheric chemistry models.

I appreciate the effort the authors took to describe the heterogeneous kinetics within a unifying framework. The introduction into the kinetics represents a nice summary of the corresponding papers by Pöschl, Rudich and Ammann [Ammann and Pöschl, 2007; Pöschl *et al.*, 2007]. Although, I am not familiar with all experimental data sets I found the representation, discussion, and final evaluation, assisted by the applied theoretical framework, fair and comprehensive. Overall, I am very supportive of the publication of this manuscript in ACP. I have a couple of minor general and specific scientific comments the authors want to consider before publication of this document.

### *Response*

*We would like to thank this reviewer for the time spent on going through this large amount of material and preparing the many useful and constructive comments.*

Regarding technical corrections: This is a long document that includes sections written by different authors, and thus exhibits in many places inconsistent formatting but also typos etc. I am giving some general comments on technical corrections below. However, instead of writing a very long list of individual page and line numbers to indicate repeated inconsistencies (in e.g. applied units etc.) or typos, for the over 350 ACPD pages, I have given these corrections as notes on top of the manuscript attached as pdf file to this review (see below). Also, specific scientific comments are indicated within the attached manuscript. I hope that this approach may speed up the correction process when using e.g. two screens/windows in parallel to find readily the places for making the corrections. In some places the corrections seem meticulous and only serve the authors to not miss out on instances when deciding to follow my suggestions.

*Response*

*We really appreciate the substantial efforts spent on pointing out all these additional typos and inconsistencies that have not already been removed in the production process for ACPD. We will go through the extensive list of corrections provided by the reviewer as annotations to the pdf document and include them in the revised version where appropriate.*

General comments:

I advise to use SI units throughout this document as defined in the beginning of the manuscript. Pressures should be in Pa or hPa and diffusion coefficients in atm cm<sup>2</sup> s<sup>-1</sup>, etc. I tried to mark all instances in which units have to be changed.

*Response*

*This evaluation follows the unit policy established over a sequence of previous evaluations, and we have decided to keep this also for this volume for consistency, meaning that we use strictly metric units and SI where appropriate. We follow common usage of several parameters in the atmospheric science community, e.g., pressure in bar, and also follow the common exceptions from SI, such as for the Henry's Law constant in M atm<sup>-1</sup> or diffusion coefficients in atm cm<sup>2</sup> s<sup>-1</sup>.*

*In the comments explaining the experimental data entries, where appropriate we even quote the values in the units as reported in the original study in order to facilitate tracking the origin of, e.g., the numerical value for the diffusion coefficients. We will add a note on our unit policy in the introduction section.*

Many of the discussed uptake processes depend on Henry's law solubility which in turn depends, in cases, on the concentration of the solute or protons (H<sup>+</sup>).

*Response*

*The Henry's Law constant is given in the form of a parameterization as function of pH if appropriate; we also provide parameters for a Sechenov equation to describe salting in or salting out effects, where appropriate.*

It has been shown that in aqueous electrolytic solutions the bulk concentration may not reflect the ion concentration at the gas-liquid interface (see e.g. [Jungwirth and Tobias, 2006] and others). This may not only affect the predicted kinetics but the overall interpretation of the underlying processes when going from gas to interface to bulk. I feel that this point may be worthwhile mentioning.

*Response*

*We will add a sentence of the specific case of halide ions at the solution – air interface, where we describe the halide solutions in the guide to the data sheet. We also consider mentioning this aspect in the comments on preferred values of the reaction of O<sub>3</sub> with halide solutions, where the surface processes are discussed.*

*We note however that this evaluation covers homogeneous liquid substrates only, which commonly have viscosities that lead to well mixed solutions. We are not considering non-uniform semi-solids in this evaluation.*

Regarding the uptake processes that involve aqueous sulphuric acid. In line with my previous point, gas uptake is affected by the Henry's law constant which in turn can depend on the proton concentration/activity,  $[H^+]$ . For a correct description of  $[H^+]$  at colder temperatures, the dissociation of  $H_2SO_4$  and  $HSO_4^-$  for supercooled temperatures must be known. Commonly the AIM model [Carslaw *et al.*, 1995; Clegg *et al.*, 1998] or other parameterizations are used to obtain  $[H^+]$  at desired temperatures (e.g. for upper tropospheric / lower stratospheric, UT/LS, conditions). However, experimentally obtained  $HSO_4^-$  dissociation degrees, using supercooled aqueous  $H_2SO_4$  droplets [Knopf *et al.*, 2003; Myhre *et al.*, 2003], are significant different than when predicted by e.g. AIM. The Pitzer ion interaction model by [Knopf *et al.*, 2003] reproduces

the experimental findings and as a consequence yields significantly different  $H^+$  concentrations (in fact larger concentrations) compared to AIM predictions at colder temperatures. (For more discussion, see also comment and reply on our study [Clegg and Brimblecombe, 2005; Knopf *et al.*, 2005].) This in turn leads to a lower solubility of trace gases such as HCl or NH<sub>3</sub>. The differences between AIM predictions and experimental data (dissociation degree, activity coefficients, water activity) are largest for UT/LS conditions. The change in solubility may affect, in cases, interpretation of the underlying kinetics/parameters and may be worthwhile to evaluate.

### *Response*

*We would like to thank the reviewer for raising this point. He refers to a study of direct measurements of the protonation state of bisulfate ion,  $HSO_4^-$  by Knopf *et al.* (2003). Based on a Pitzer ion interaction model, a new formulation for the acid dissociation constant is derived, and several solution parameters are compared to the AIM model (<http://www.aim.env.uea.ac.uk/aim/aim.php>; Carslaw *et al.* 1995). Knopf *et al.* find significant differences in the degree of dissociation of bisulfate ion, which will be helpful for improving the thermodynamic models by taking into account more accurate ion activities. Knopf *et al.* also derive significant deviations in water activity for more dilute solutions below 200 K. For concentrated solutions, the water activity is similar to the AIM model. The proton activity is predicted lower at  $T < 200$  K in dilute solutions, and a factor 2-3 higher at all  $T$  for more concentrated solutions than in AIM. The higher proton activity may lead to lower predicted HCl solubility.*

*Based on a follow up discussion (Clegg *et al.*, 2005; Knopf *et al.*, 2005), the significance of the revised formulation of bisulfate ion dissociation for water and proton activities within the range of conditions, where experimental data are available, and above the ice saturation line, has remained open.*

*In this evaluation, observed equilibrium and kinetic data are parameterized as a function of sulfuric acid weight percent used in the experiment in most cases. Only in a few cases, the experimental studies were performed at prescribed water activity so that the solution composition had to be derived from a parameterization of water activity. We therefore refrain from changing the description of water and proton activity, but add text mentioning this discussion to the introduction text describing the sulfuric acid solution properties. We agree with Knopf *et al.* and Clegg *et al.* that this discussion need to flow into future improvements of the thermodynamic models.*

*For some reactions, some of the rate constants have been parameterized as a function of proton activity in our evaluation. In those cases we will add an additional caveat to the*

*individual datasheets and eventually increase the uncertainty of the rate constants, if appropriate.*

This compendium does not systematically evaluate the effect of organic coatings (mono- or multilayers of organic molecules) at the gas-liquid interface on the uptake of trace gases. For some cases (inconsistent), the authors mention very briefly the effect of a coating. I suggest discarding this information from the manuscript or if included, to evaluate all studies that investigated uptake of trace gases by water and aqueous solution surfaces coated by organic material. My feeling is that this would be beyond the scope of this manuscript. Furthermore, a coating or presence of an organic monolayer at the gas-liquid interface and its effect on the underlying kinetic parameters of the unifying framework may need more attention than it is given currently here (possibly inclusion of another layer with additional accommodation coefficients etc.). As is, the previous literature is not represented in a balanced way and thus I recommend omitting the few cases in which the authors mention the effect of organic coatings and focus solely on purely aqueous substrates.

*Response*

*We agree that this evaluation cannot consider the effect of organic coatings explicitly and in full. We believe that it is important to mention that coatings may have an effect on uptake. However, we do not provide a recommendation with respect to their quantitative effect on uptake. We will add text in the introduction text to indicate this.*

*Since this topic has found special attention in the literature in the context of  $N_2O_5$  uptake, we will add a caveat to each of the relevant  $N_2O_5$  datasheets that in the atmosphere uptake may be different due to complex composition and provide a general reference that discusses such effects (Abbatt et al., 2012).*

Specific comments (see also remarks within manuscript pdf file):

After Eq. 6: Maybe I am missing the obvious, but I do not entirely understand lines 9-12. I think it would be helpful to explain from where comes the definition of  $k_{des}$ ? With  $B$  given, is it trivial to see that the characteristic time is  $1/k_{des}$ ? Which equilibrium is meant? I do not see readily how  $\gamma$  drops to zero with the information given. Please briefly elaborate on this section; this would be helpful for the reader.

*Response*

*The confusion likely comes from a typo in the conditional expression in line 9 on p32120: Low coverage means that the desorption rate constant  $k_{des}$  is much larger than the adsorption rate constant,  $\alpha_s(c[X]_g)/4N_{max}$  (not equal). Then it is immediately clear that  $B$  is dominated by the constant  $k_{des}$  and determines the time dependence of  $\gamma$  as in equation (5). Will be corrected.*

After Eq. 16: "Equation (16) demonstrates that  $\gamma$  depends on the gas phase concentration of  $X$ , if  $KLangC(X)[X]g$  is similar to or larger than 1 (i.e., at high coverage)." I am not sure if a reader not as familiar with the resistance model can understand this statement. Maybe it would help to give the relationship between  $\gamma$  and  $\Gamma_s$ .

*Response*

*We agree, it is not directly apparent how  $\gamma$  is obtained at this point. We will modify equation (16) to:*

$$\frac{1}{\gamma} = \frac{1}{\alpha_s} + \frac{1}{\Gamma_s} \quad \text{with} \quad \Gamma_s = \frac{4k_s [Y]_s K_{LangC}(X) N_{\max}}{\bar{c} (1 + K_{LangC}(X) [X]_g)}$$

The summary sheets have inconsistent/missing formatting in terms of species phase state indication. E.g. “H<sub>2</sub>O (l)” and not “H<sub>2</sub>O(aq)” etc. Also, some reactions (and corresponding titles in the appendices) do not show the correct stoichiometric coefficients. Details are pointed out in manuscript file.

*Response*

*we will check through all phase indices and reaction stoichiometries.*

Table 1 could include the reacto-diffusive length as a parameter.

*Response*

*This is a good point, and we will include this parameter in the table.*

For the case of N<sub>2</sub>O<sub>5</sub> uptake by aqueous H<sub>2</sub>SO<sub>4</sub> our uptake study could be included [Knopf et al., 2007] (if the authors feel it benefits the manuscript). N<sub>2</sub>O<sub>5</sub> uptake by aqueous H<sub>2</sub>SO<sub>4</sub> solution 60 and 80 wt% in concentration was determined using a rectangular channel flow reactor (RCFR) coupled to CIMS correcting for changes in the N<sub>2</sub>O<sub>5</sub> profile due to uptake (i.e. accounting for diffusion effects) in flow and lateral direction.

*Response*

*We agree that these data should be included and will amend the datasheet.*

Technical Corrections:

There are many places in which technical corrections are needed for reasons of keeping consistency or correction of typos etc. Those are marked in the manuscript pdf-file.

*Response*

*Thank you for pointing all these out. We will carefully consider all your suggested changes.*

A few general statements regarding technical corrections:

Keep document either in British or American English.

*Response*

*We will check with the editorial office regarding some of the technical, language and math issues in the process of production of the final version of this volume.*

Keep format of “Experimental Data Table” and “Preferred Values Table” similar. E.g. “T/K” etc.

*Response*

*We will check and harmonize these again.*

Keep concentration format consistent, i.e. "molecule cm-3" and not "cm-3", "molecules cm-3", or "atm".

*Response*

*We will check and harmonize these.*

I suggest using the mathematical symbol "times", i.e. "x" only when expressing the exponent as when giving concentrations but not in mathematical equations (this would indicate a cross product). For the latter application, please use a center dot.

*Response*

*We will try to reduce the usage of the multiplication sign and also consult with the editorial with respect to their policy on this subject.*

When giving parameter ranges, make sure exponent and units are at the correct place. The formatting is very inconsistent throughout the manuscript. E.g. (1-5)x10-5 molecule cm-3.

*Response*

*We will check and make sure that such ranges are correctly formatted.*

## References

Abbatt, J. P. D., Lee, A. K. Y., and Thornton, J. A.: Quantifying trace gas uptake to tropospheric aerosol: recent advances and remaining challenges, *Chem. Soc. Rev.*, 41, 6555-6581, 2012.

Carslaw, K. S., Clegg, S. L., and Brimblecombe, P.: A thermodynamic model of the system HCl-HNO<sub>3</sub>-H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O, including solubilities of HBr, from <200 to 328 K, *The Journal of Physical Chemistry*, 99, 11557-11574, 1995.

Clegg, S. L., and Brimblecombe, P.: Comment on the "Thermodynamic dissociation constant of the bisulfate ion from Raman and ion interaction modeling studies of aqueous sulfuric acid at low temperatures", *J. Phys. Chem. A*, 109, 2703-2706, 10.1021/jp0401170, 2005.

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