Review: **Evaluated kinetic and photochemical data for atmospheric chemistry: Volume VI – heterogeneous reactions with liquid substrates by M. Ammann, R. A. Cox, J. N. Crowley, M. E. Jenkin, A. Mellouki, M. J. Rossi, J. Troe, and T. J. Wallington**

General: This is another chapter in the highly reputated IUPAC recommendations which are an indispensable tool for anybody dealing with atmospheric chemistry. I think, first of all, the authors and especially Markus Ammann as the lead author should be gratulated to tackle not only gas phase reactions as before, but also, heterogeneous reactions and now heterogeneous reactions with liquid substrates.

The paper very early lists the recommended values and then discusses the different physicochemical steps which can occur when gases interact with liquid particles. This part is clear and in my opinion can serve as a reference text as it stands for the basics and the model frame which it addresses.

My general feeling is that this evaluation can be very helpful for our field of science but certain improvements of the treatment are still possible. Needless to say that an IUPAC recommendation has a very strong weight and impact in our field of science. Recommended data will shape the use pattern of parameters enormously and will strongly influence model development. Non-recommened data naturally will be used less or not at all any more. Moreover, the IUPAC recommendations will also steer further experimental work as the hurdle to start another investigation on a system where an evaluation exists becomes higher – I am afraid that then high-ranking evaluations maybe even could suppress the undertaking of more independent experimental studies – this would be natural, if the recommendations are on a broad basis and cannot easily be shattered. However, if the basis is not broad enough, the greatest care should be taken in giving recommendations.

Within the evaluation, it is assumed that for the systems discussed a clear recommendation can be given at the time of writing. I would like to ask the committee to evaluate again if this is really the case – I am regarding this point as rather critical. For some systems large uncertainties exist, and then the front text might promise a too optimistic view on the current state of science with regard to the available uptake and mass accommodation coefficients for transfer into aqueous systems. My feeling is that for some systems this state has not been reached yet, in particular, **I do see the need for more independent experimental work for the following sub-systems, just to name some:**

- **VI.A1.1 $O_3 + H_2O_{(l)}$**
- **VI.A1.3 $2\ NO_2 + H_2O$ (l) (discussed) vs $NO_2 + H_2O$ (not discussed)**
- **VI.A2.05 $NO_3 + Cl^- / Br^- / I^-$**
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It would be very helpful to make the criteria public which the committee thinks it allows recommendation – I feel sometimes the data basis is just not broad enough for a recommendation – Please compare to the gas phase chemistry situation. Shouldn’t several independent experimental determination, preferably performed with different experimental techniques result in a consistent range of the observable which only then can be recommended ? Please double-check all systems for this. Openly name the criteria which did enable you to recommend data. Is a single self-conclusive study enough to do so ?

I would like to suggest to not leave systems out where only few contradicting values exist but to label them clearly and recommend further experimental work.

When dealing with this comment it would also be helpful, in the general part to review the available experimental techniques and to evaluate them. Within the single system evaluation annexes, then the reader can be referred back to this part. Apparently, some of the experimental techniques are bearing problems in view of the evaluators, but then this has to be clearly outlined, to my feeling in front of the annexes.

When going through the single systems, I have some concerns, however, which I am listing below in detail. I do recommend that the formal aspects (such as the headings which are different all the time, please pay attention to proper phase indices) should be treated more clearly and in a uniform way. Numbering is also still not correct. VI A2.02 is followed by VI A2.04., hence please double check all heading and numbering and turn it consistent.

It would be good to state in text form when a mass accommodation coefficient can be recommend and when ‘only’ an uptake coefficient is given. Such clarification statement should be done in front of the small recommendation Tables in each system section. Here, it would also be good to state if (lower) limits are given rather than mean recommended values with their error range. These one or two sentences could introduce the “Preferred values” tables throughout.

Another, different aspect: My feeling is there are more measurements, e.g. for the uptake of carbonyl compounds, available which are not covered in this evaluation. Maybe a Table can be given for an overview ? If this is right, what is the reason for not covering them ?

To conclude this general section, I would like to again state my highest appreciation for the effort of the group.

Details

Remarks to Section 2 - Summary sheets

Please see my general comments.

Remarks to section 3

Please see my general comments.

Remarks to the Datasheets

I am going through the single systems in the following. Only those are listed where I have remarks.

Appendix A1 – Uptake on liquid water surfaces

VI.A1.1 $O_3 + H_2O_{(l)}$

The Schütze und Herrmann value is not inconsistent with the recommended lower limit of Magi et al. The concern on the iodide-ozone reaction is valid.

VI.A1.3 $2\ NO_2 + H_2O_{(l)}$

This is an interesting compilation, but what happens, if the NO_2 gas phase concentration becommes low, so that the bimolecular reaction becomes highly improbable ? I think, the reaction $NO_2(g) + H_2O$ (l) -->, i.e. just the physical uptake, should also be discussed.

VI.A1.4 NO_3 + H2O $_{(aq)}$

Heading: Up to here, the water in the reactions is always labelled H2O(l) but here it is H2O (aq) - Shouldn't this be H_2O(l) here as well ?

Page 32159: The reaction of NO3 with water is thermodynamically not feasible, and this has been discussed in literature, cf. Herrmann et al (2003)

This might be a case where the state of knowledge is so limited that no recommendation should be given.

VI.A1.5 $N_2O_5 + H_2O$ (water droplet)

Heading: Now, 'H_2O (water droplet)' is used, why not H_2O (l) ? If this indexing of H_2O should stay like this, a section about it should be introduced in the front text and clearly define the indexing.

VI.A1.7 $HNO_2 + H_2O_{(l)}$

Heading: H_2O (l) again, but the chemical reaction is imbalanced. I do not think that the uptake of HONO on pure water can be written like this. H_2O (l) occurs on both sides of the equation. If the bimolecular reaction is referred to, it need to be written like this, cf. remark (f), page 32170. If this is the case, as in the case of NO_2, the monomolecular uptake needs to be discussed separately.

VI.A1.8 $HNO_{3(g)} + H_2O_{(l)}$

Heading: Here it is again H_2O (l). The reaction is imbalanced, H_2O (l) should be added on the right side.

VI.A1.9 $CH_3SO_{3(g)} + H_2O_{(l)}$

Heading: Here it is again H_2O (l), could as well be H_2O (water droplets). Please clarify. The reaction is imbalanced, H_2O (l) should be added on the right side.

VI.A1.10 $SO_{2(g)}$ + $H_2O_{(l)}$

Heading: H_2SO_3 is probably not existing as a molecule, see inorganic chemistry textbooks.
I think this should better be written as: $SO_{2(g)}$ + H2O (l) --> $SO_{2(aq)}$ + H_2O(l)
The recommendation at the end of the section should be clarified. As the authors state that the equation in line 11 is a proper description. the needed parameter should (again) be compiled in an table close to the equation for better applicability.

The text on this very important system leaves the reader a bit unsatisfied. What is recommended ? Should rather the equation on the bottom of page 32187 be applied or is α =1 a good approximation to it ?

VI.A1.11 HCl + $H_2O_{(l)}$

Heading: HCl is given without a phase index. I would recommend to alöway give them, cf. the NO_2 system VI.A1.3 2 NO_2 (g) + H_2O (l). I think in this system the product can be written as HCl(aq) which subsequently dissociate. This does also apply to the following two systems.

VI.A1.12 HBr + $H_2O_{(l)}$
The same comments apply as for VI.A1.11

VI.A1.12 HI + $H_2O_{(l)}$
The same comments apply as for VI.A1.11

VI.A1.14 ClNO $_{(g)}$ + $H_2O_{(l)}$ --> $H^+_{(aq)}$ + $Cl^-_{(aq)}$ + $HNO_{2\ (aq)}$

Heading: All phases indices given, this should consistently always be done like this.

Recommendation: There is a typo, the reliability must be Δ log (γ), not Δ log (α).

VI.A1.15 $ClNO_{2\ (g)}$ + $H_2O_{(l)}$ --> products

Heading: As the products are unclear, this is ok.

VI.A1.16 $ClONO_2$ + $H_2O_{(l)}$ --> HOCl + $HONO_2$

Heading: Here it is very important to carry the correct phase indices. The product are expected to be gas phase, however, this has not been detected in the study by Deiber et al.

Page 32202, line 9: "No gas phase product were detected. This can be confusing - did the author try to measure them and did not see them or wasn't it tried - I think the latter is true.

VI.A1.17 OH $_{(g)}$ + $H_2O_{(l)}$ -->

Heading: Add products to the right.

As this mass accommodation coefficient is important for all atmospheric aqueous phase radical chemistry, I see a slight discrepancy between the text and the preferred values Table.

I guess the text give various indications that a is probably close to 1 - Then: Isn't $\alpha > 0.1$ too low as the lower limit ?

VI.A1.18 $H_2O_{(g)} + H_2O_{(l)}$ --> 2 $H_2O_{(l)}$

Heading: Add a phase index at the first H2O for more clarity.

VI.A1.19 SO_2 + $H_2O_{2\,(aq)}$ --> $H_2SO_{4\,(aq)}$

Heading: Add a phase index for SO2.

It would be nice to perform a comparison whether the observed uptake onto H2O2 solution is consistent with the uptake of SO2 followed by the very well characterised aqueous phase oxidation of dissolved S(IV) by hydrogen peroxide. Martin and Damschen is a classical work but only one out of many studies on this system......

VI.A1.20 HO_2 + $H_2O_{(aq)}$ --> products

Heading: Check phase indices, specify products.

This system should be treated consistently with the uptake of OH. Here, quite a high value is recommended, even as the actual measurement is low. In the OH case, a low lower limit is recommended even if the experimental determination indicates α near unity.

A lot of aqueous phase chemistry can go on involving HO2 and its conjugate base O2-.

The recent study of Mao et al. should be referenced. Role of TMI.

Appendix A2

VI.A2.0 $O_3 + Cl^- / Br^- / I^-$ --> products

Heading: Should be '$O_{3\,(g)}$' and $X^-_{(aq)}$
I wonder why these three systems should be put together and would like to recommend separate treatment, it could be a s VI.A2 0 (a), …(b) and (c)
What is the situation for the Ozone + cloride system ?
Why is the numbering starting here with '0' ?

VI.A2.1 OH + aqueous sea salt aerosol --> products

Heading: Check phase index of OH

General comment : The finding from the Finlayson-Pitts group is rather controversely discussed. What about chamber wall effects affecting this work ?

Check the numbering of the system , is it '01' or '1' ? Please number uniformly.

VI.A2.02 $HO_2 + Cl^- / Br^- / I^-$ --> products

Here the dissolved halides will not influence the decay of HO2 / O2-. This shoul dbe stated more cleary and early in the text. The mass accommodation thus need to be identical to pure water. Please clarify if this system merits a recommendation then. Add cross reference.

VI.A2.04 $NO_{2\ (g)}$ + aqueous sea salt aerosol --> products

This section has the wrong number. Hence the follwing section numbers in A2 are also not correct.

VI.A2.05 $NO_3 + Cl^- / Br^- / I^-$

Heading: Please check phase indices.

Again, the three halides should be treated separately.
I think this system warrants further study. See Herrmann (2003). I do not think the system used by Schütze et al. (2005) was disturbed by 'large impurity levels of HNO3'.

For the remaining part of A2 I have no more detailed comments except please check all headings and correct the numbering.

Appendix A3

Why is the first section in A3 labeled ' VI.A3.5 and not '1' in its last digit ? So, eventually, the sections in A3 could be re-numbered. Check phase indices again.

Appendix A4

Here, the first section is 'VI. A4.0' – shouldn't it start with '1' ?

For the whole section: **Heading:** Please check phase indices. E.g. compare the heading of VI.A4.0 with the one of VI.A4.1 – I do suggest to carry phase indices all the time like in the latter heading. Please check.