

Response to the review comments by H. Herrmann

M. Ammann, R. A. Cox, J. N. Crowley, M. E. Jenkin, A. Mellouki, M. J. Rossi, J. Troe, and T. J. Wallington

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

General: This is another chapter in the highly reputed 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.

Response

We would like to thank this reviewer for the thorough reading and the constructive comments. Indeed, this evaluation has a significant history and the diversity of the heterogeneous or multiphase reactions has been a challenge to the whole task group.

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-recommended 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.

Response

We agree and actually hope that the endeavors of the task group to evaluate and present existing experimental data in a harmonized way will lead to further experimental work and possibly also act as a guide to future studies. However, we also believe that even the basic concepts will have to be continuously evaluated for their applicability based on future data and systems. Therefore, we agree that improvements from both the conceptual side and from the side of systems covered will always be possible. We do not think that the IUPAC evaluations will inhibit future experimental work (or that they have done so in the past). Rather, by identifying areas of uncertainty, we expect that the evaluations will aid experimentalists in atmospheric research to conduct experiments that have significant

impact. Especially for heterogeneous kinetics, our evaluations clearly show that substantial uncertainties still exist in many key processes that warrant further investigation.

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.

Response

We will add a few more statements in the introduction section to the guide of the datasheet to more clearly express the purpose of this evaluation, the selection of systems evaluated and some of the guiding principle that leads to preferred values.

The tabulated list of preferred values (referred to by the reviewer as the front text) is necessary as it provides a quick and simple overview of what systems have been covered. It is also directly apparent from these summary tables that for many reactions, not for all parameters preferred values are given, indicating lack of data or coverage of necessary parameter space in the available experimental datasets. The details including the breadth of the dataset upon which the preferred values are based and how the uncertainty is assessed cannot be provided here. However, anyone requiring information in any particular process is encouraged to read the individual datasheets in which extensive notes on the preferred values and the levels of uncertainty are indicated. We emphasise that many parameters are preferred with substantial uncertainty encouraging further experimental work.

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 $\text{O}_3 + \text{H}_2\text{O}$ (I)**
- **VI.A1.3 $2 \text{NO}_2 + \text{H}_2\text{O}$ (I) (discussed) vs $\text{NO}_2 + \text{H}_2\text{O}$ (not discussed)**
- **VI.A2.05 $\text{NO}_3 + \text{Cl-} / \text{Br-} / \text{I-}$**
-

Response

We agree that further work is desirable in many cases. Note that the panel never suggests that further experimental work is NOT necessary, not even in the evaluation of gas-kinetic data for which more than 10 independent studies are available. In our datasheets we use the term “preferred values” rather than “recommendation” which does not carry any implications for the quality (or finality) of the dataset(s) but simply reflects the present state of the data. The preferred value is based on a consideration of applicability of experimental method, coverage of parameter space (T , partial pressure gas phase species, humidity, concentrations in the condensed phase), within the atmospherically relevant range of variability. We recognize that the preferred value can change with publication of new data

and this is why we keep the option to update the web-site at higher frequency than publishing in ACP.

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 determinations, 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.

Response

Ideally, for any particular process, we would like to have several independent studies using different methods. In heterogeneous kinetics this is seldom the case. If only one study is available we base our preferred values on this study if the method and experimental conditions are appropriate to enable application (or, when necessary, extrapolation) to the atmosphere. If two studies on a single process disagree beyond reasonable uncertainty, we base our preferred values on the breadth, coverage of the dataset and differences (if any) in the methods. Such situations are usually discussed in detail in our text related to the derivation preferred values. The general approach and methods used have also been reviewed recently by Cox (2012). We will add further explanations on our evaluation method to the introduction text of the guide to the datasheets in the revised version.

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.

Response

We do not fully understand what is meant by “leaving out systems”. We do not leave out reactions on purpose. We may not list preferred values in a case where contradictory data exist, if the basis for giving a preferred value as described above is not available. The selection of heterogeneous processes covered has a focus on those relevant for the stratosphere and the marine boundary layer. It is far from complete. This volume is a compilation of what has been evaluated by the panel to date, and is not intended to cover all heterogeneous reactions with liquid substrates. This is a practice similar to all previous evaluations, gas phase or heterogeneous.

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.

Response

Some techniques are more (or less) suitable to study any single heterogeneous process or a certain parameter implicated in it. A description of the advantages and disadvantages of any one technique cannot therefore be given independently of the process being studied.

Different techniques give access to different parameter space, no single one is ideal. We make a general statement that where available methods using aerosols should be preferred over those using less relevant surfaces, but this cannot be over generalized.

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.

Response

We will go through all datasheets again and check for consistency of phase indices and reaction stoichiometry etc.

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.

Response

The numbering is indeed correct. It just means that the datasheet with the identifier VI A2.03 has been reserved for other processes not yet evaluated.

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.

Response

In line with future developments of the IUPAC database, the preferred value tables purposely contain only numbers or mathematic expressions in order to remain in machine readable format. Whether a bulk accommodation coefficient or an uptake coefficient is given is clearly apparent from the symbol used in the parameter column. Upper or lower limits are clearly apparent from the table. All further comments and discussion of the content of the table are given in the text immediately following the tables.

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 ?

Response

As mentioned above, this evaluation covers only a subset of all potential systems. Indeed we have not tackled organics (neither as gas phase species nor as substrate), except in the form of carboxylic acid substrates for N₂O₅ hydrolysis. This publication is limited to systems we have evaluated until dec 2012. Further systems will be evaluated in the future and published in future volumes when warranted. The summary sheet should actually represent the

overview table listing all reactions evaluated. Statements will be added to the introduction text to explain the selection of systems for this volume.

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 O₃ + H₂O (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.

Response

Correct. We will amend the corresponding sentence to: The data by Schütze and Herrmann (2002) are more strongly affected by diffusion, and the model to take that into account required several simplifications; their lower limit to α_b is however consistent with that by Magi et al.

VI.A1.3 2 NO₂ + H₂O (l)

This is an interesting compilation, but what happens if the NO₂ gas phase concentration becomes low, so that the bimolecular reaction becomes highly improbable ? I think, the reaction NO₂(g) + H₂O (l) -->, i.e. just the physical uptake, should also be discussed.

Response

As discussed in detail in the comments to the preferred value, dissolution (physical uptake) and disproportionation cannot be easily separated. In that sense, the kinetic data provide a constraint on $Hk^{1/2}$, and only careful separation of solubility limited from reaction limited regimes allow estimates of the two individually. At the end, we also provide a value of the uptake coefficient due to reaction and caution that the geometry (small particle, or droplet, or film in case of a lab experiment) play a role, and also that uptake may be limited by solubility only. Depending again on geometry, solubility limited uptake (i.e., physical uptake) is time dependent; therefore, an extended discussion is probably not adequate there. The datasheet (with the help of the equations in the guide to the datasheet) clearly allows calculation of the kinetics under all conditions. We will therefore only modify the text to the extent as to mentioning the time and geometry dependence in the expression for Γ_{sol} .

VI.A1.4 NO₃ + 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 H₂O(l) here as well ?

Response

Yes, indeed, we will correct this.

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.

Response

We recognize that there are severe discrepancies and discuss these in detail. We take a pragmatic approach and write: "Whilst recognising that there is very large uncertainty associated with values of each of α_b , H and k_{H_2O} , we adopt the results of Rudich et al. (1996) so that the following expression, when used to calculate an uptake coefficient for NO_3 on pure water, returns a value of $\gamma \sim 2 \times 10^{-4}$, which is consistent with their experimental observations." We also write that "We prefer the results of Rudich et al., in order to maintain an internally consistent set of parameters for modelling NO_3 uptake to both pure water and halide solutions (see VI.A2.05)"

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

Heading: Now, 'H₂O (water droplet)' is used, why not H₂O (l) ? If this indexing of H₂O should stay like this, a section about it should be introduced in the front text and clearly define the indexing.

Response

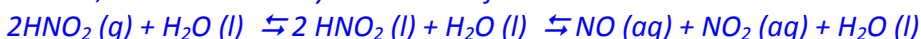
We will make sure that phase indexing remains consistent throughout.

VI.A1.7 $HNO_2 + H_2O$ (l)

Heading: H₂O (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. H₂O (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 NO₂, the monomolecular uptake needs to be discussed separately.

Response

Correct, the stoichiometry needs to be fixed. The title reaction will be modified to:



The reason for keeping dissolution and decomposition for this system together is similar to that of NO₂. The decomposition process is intricately linked to physical uptake, and so is acid dissociation, and all experiments targeting the solubility have to take this into account. Since the system is further complicated by the reaction of NO(aq) with NO₂(aq) back to HNO₂(aq), we cannot provide an expression for the uptake coefficient, and the system needs to be solved explicitly. This point is already mentioned on p32172, line 11-12.

VI.A1.8 $HNO_3(g) + H_2O$ (l)

Heading: Here it is again H₂O (l). The reaction is imbalanced, H₂O (l) should be added on the right side.

Response

Correct, will be added.

VI.A1.9 CH₃SO₃(g) + H₂O (l)

Heading: Here it is again H₂O (l), could as well be H₂O (water droplets). Please clarify. The reaction is imbalanced, H₂O (l) should be added on the right side.

Response

Correct, will be added.

VI.A1.10 SO₂(g) + H₂O (l)

Heading: H₂SO₃ is probably not existing as a molecule, see inorganic chemistry textbooks.

I think this should better be written as: SO₂(g) + H₂O (l) --> SO₂(aq) + H₂O(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 $\alpha = 1$ a good approximation to it ?

Response

We agree that the presentation of this datasheet could be improved, including the formulation of the chemical reaction. We will amend the text by first introducing the surface complex, then discussing bulk accommodation and the further aqueous phase processes. We will make sure that the expression for calculating the uptake coefficient and the parameters contained in it will be presented in clearer form.

VI.A1.11 HCl + H₂O (l)

Heading: HCl is given without a phase index. I would recommend to always give them, cf. the NO₂ system VI.A1.3 2 NO₂ (g) + H₂O (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.

Response

The phase index will be added, but we have decided not to include acid dissociation in the title reactions.

VI.A1.12 HBr + H₂O (l)

The same comments apply as for VI.A1.11

Response

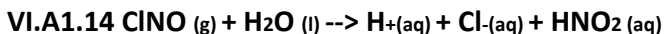
dito

VI.A1.12 HI + H₂O (l)

The same comments apply as for VI.A1.11

Response

dito

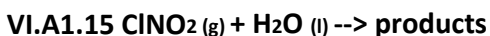


Heading: All phases indices given, this should consistently always be done like this.

Recommendation: There is a typo, the reliability must be $\Delta \log (\gamma)$, not $\Delta \log (\alpha)$.

Response

Actually, the uncertainty of γ must be added, $\Delta \log (\alpha_b)$ will remain. Also, for consistency, the title reaction will be changed to include HCl (aq) rather than the dissociated products.



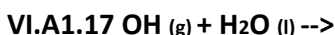
Heading: As the products are unclear, this is ok.



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.

Response

We will amend the description in the revised version to clearly state that they have not analysed these products and only mention in the discussion of the preferred values what other evidence is available that these products are formed.

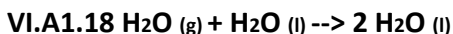


Heading: Add products to the right.

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 α is probably close to 1 - Then: Isn't $\alpha > 0.1$ too low as the lower limit ?

Response

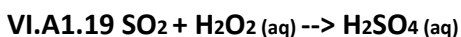
Since none of the experiments was directly sensitive to α_b , we remained cautious in the recommendation. Our recommendation is already a factor of ten above the largest observed uptake coefficient. As mentioned in the comments, the uncertainties in the rate constants of the four reactions and in the solubility lead to significant degrees of freedom to adjust the kinetics to the measured γ values. It is clear from the given uncertainty and the comments that sensitivity studies should consider the range up to 1. We will add a short discussion of the uncertainty to emphasise this.



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

Response

Ok, will be done



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.....

Response

Ok, phase index for SO₂ (g) will be added.

We emphasise that our evaluation is not a complete evaluation of aqueous phase kinetics (will also be included in the introduction text), but constrain ourselves to studies that have quantified gas uptake kinetics. We are of course aware of many older kinetic studies of this liquid phase reactions. We will insert the following paragraph to set the scene for our choice: 'The oxidation of sulphur dioxide gas by hydrogen peroxide in aqueous droplets has been recognised as an important process for production of sulphates following studies of the reaction kinetics in the late 1970s (Hoffmann and Edwards, 1975; Penkett et al, 1979; Martin and Damschen, 1981). However direct measurements of SO₂ gas uptake kinetics to determine γ values were not achieved successfully until the improvements in experimental techniques for multiphase atmospheric processes in the late 1980s.'

VI.A1.20 HO₂ + H₂O (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.

Response

In this case the higher recommendation is related to experiments on other aqueous (halide) solutions with added Cu(II), which led to measured uptake coefficients around 0.1. We therefore transfer that recommendation for the halide solutions to the 'pure' water case here. Based on just the data for 'pure' water, we would have to keep $\alpha > 0.01$. We will add a remark and cross reference to the corresponding sheets to make this clear. In general, the data base for HO₂ is quite different in quality, range of methods and coverage of parameter space than that for OH. We will also mention the recent study by Mao et al. (2013), which does not contain new experimental data though.

Appendix A2

VI.A2.0 O₃ + Cl⁻/ Br⁻ / I⁻ --> products

Heading: Should be 'O₃ (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 + chloride system ?

Why is the numbering starting here with '0' ?

Response

Numbering of the gas phase species is not meant to be consistent on the different substrates. Phase indices will be added.

Due to the convolution of the treatment we have decided to keep the reaction of O₃ with bromide and iodide on one single datasheet, but to delete chloride from the title reaction, since we don't evaluate the aqueous phase chemistry of chloride with O₃, and the slow kinetics of the process has likely not affected any of the O₃ uptake experiments with halide solutions.

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 controversially discussed. What about chamber wall effects affecting this work ?

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

Response

Phase indices will be added, and the numbering changed to VI.A2.01 to be consistent in format with the others; the title reaction could be changed to OH(g) + Cl⁻(aq) -> 0.5 Cl₂ + OH⁻ to keep the focus on this process.

The possibility of wall effects is a valid point. A caveat will be added. The uncertainty given for the surface process is already quite large and will remain.

VI.A2.02 HO₂ + Cl- / Br- / I- --> products

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

Response

The recommendation for the bulk accommodation coefficient was based on the experiment with added Cu(II) as scavenger and indeed forms the basis for the recommendation for pure water. Cross references will be added to both datasheets.

The predominance of the self reaction is mentioned in line 13 on p32236. We will extend the sentence to say that halide ions are not reacting directly with HO₂.

VI.A2.04 NO₂ (g) + aqueous sea salt aerosol --> products

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

Response

The number is correct. As mentioned above, NO₂ has not a consistent end number on the different substrates.

VI.A2.05 NO₃ + 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'.

Response

The datasheet uses only three different rate coefficients to present a unified parameterization of all systems. We think it appropriate to treat these reactions together as they all require the same bulk accommodation coefficient, hydrolysis rate coefficient, solubility and aqueous-phase diffusion coefficient.

In comment (c) we write that "HNO₃ was formed at ≈ the same concentration as NO₃." This information was given by the authors. Taking the relative solubilities of NO₃ and HNO₃, this can be considered a significant impurity (making aqueous phase nitrate).

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

Response

We will check all title reactions and phase indices.

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.

Response

Identifiers VI.A3.01-04 reserved to other processes not yet evaluated.

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.

Response

We will check all title reactions and phase indices.

Reference

Cox, R. A.: Evaluation of laboratory kinetics and photochemical data for atmospheric chemistry applications, Chem. Soc. Rev., 41, 6231-6246, 2012.

Mao, J., Fan, S., Jacob, D. J., and Travis, K. R.: Radical loss in the atmosphere from Cu-Fe redox coupling in aerosols, Atmos. Chem. Phys., 13, 509-519, 2013.