Referee 2

General comment

The submitted article represents an enormous undertaking on the part of the authors to catalog, sort and evaluate a huge number of studies related to heterogeneous uptake of important atmospheric trace gas species onto relevant aerosol surfaces. It will certainly serve as the definitive reference for many, if not all, future laboratory studies of heterogeneous chemistry of significance to atmospheric processes. Hopefully, the results presented here become of interest and use to scientists involved in climate and chemistry modeling. The detailed comparisons and expert commentary may facilitate the incorporation of these laboratory results into more sophisticated models of atmospheric chemistry. The quality and detail of the work are excellent and the presentation, especially with the detailed evaluative notes, is very good..

Reply

None required

Specific Comment

There were a few issues I thought might have been addressed more thoroughly, or perhaps a little differently, in the background material of section 3. The presence and amount of atmospheric water is one of the most critical environmental determinants in uptake kinetics and partitioning. In some systems, RH acts to facilitate uptake and surface reaction and in other systems water adsorption is competitive with trace gas uptake. Many of the results in the tables are for low pressure experiments with negligible or very low RH, conditions which are not relevant for tropospheric processes. For example, the preferred value for O_3 uptake is for RH values below 5% which is not relevant for the troposphere. I thought this might have been discussed in a little more detail. I do see a lot of information about RH and some parameterizations in the appendices, however.

Reply

Agreed, the role of water vapour could be emphasised more. We add some text (red below) outlining the role of surface H_2O in section 2, on page 5243.

A proper description of the interaction of a trace gas with a surface would include transport to and accommodation at the surface, followed by a number of competitive or parallel processes such as desorption back to the gas phase, reaction with the substrate surface or with other trace gases on the surface, and diffusion into and reaction in the particle bulk (important for liquid aerosol; less so for solid particles). The rates and efficiencies of these processes are controlled by surface and bulk-phase rate coefficients, local reactant concentrations, diffusion coefficients in the condensed phase, and solubilities. Each of these controlling factors may change with temperature and composition. The role of surface adsorbed H_2O is especially noteworthy as it can both accelerate and slow down rates of trace gas uptake and can be a rate determining parameter in some systems. When appropriate we prefer experimental results in which atmospherically relevant relative humidities prevailed, especially when dealing with non-ice surfaces (e.g. mineral dust). In short, atmospheric heterogeneous processes can be highly complex.

Specific Comment

The discussion of mineral dust was confusing in the presentation. At first, I thought the contention was that only studies on authentic dusts were to be included which I found questionable from the standpoint of heterogeneous chemistry. A number of atmospheric chemistry models account for a degree of heterogeneity in the aerosol population. There was also no discussion of the potential differences in the authentic" dust samples, unlike the discussion of the details of ice formation. As far as I can tell there is no accepted protocol for collecting, storing and preparing these samples and from experience, the methods employed are sometimes pretty crude (perhaps necessarily so). On the other hand, commercial samples of mineral dust components are generally reproducible and well characterized. There have been at least some attempts to model the reactivity of actual dusts from a consideration of the reactivity of the individual components. Again, I do see many studies in the appendices that use model dust surfaces.

Reply

Our text reads "Recognizing that synthetic oxides do not necessarily mimic the reactivity of natural dust, our preferred values are presently based on experiments using Saharan or Asian dust samples, preferably presented in aerosol not bulk form."

We recognise that most of the studies listed in the section on mineral dust have indeed not used "authentic" samples. However, an uptake coefficient measured on a substrate that represents only 1-10 % of the mineral dust mass is unlikely to deliver a result that can be directly transferred to a model of the atmosphere. Note that many of the datasheets covering mineral dust do not produce a preferred value as either the experimental method and conditions, or choice of mineral oxide were not conducive for the generation of reliable data which could be used in a model. In short, having received relatively little experimental attention, the database on mineral dust is not in such good shape as e.g. is the case for ice. It seems that the safest bet (at the moment) is to rely on data that has been obtained using Saharan or Asian dust, which represent the greatest contribution to atmospheric dust loading. We shall modify the text slightly to read "Recognizing that synthetic oxides do not necessarily mimic the reactivity of natural dust, where possible our preferred values are presently based on experiments using Saharan or Asian dust samples, preferably presented in aerosol not bulk form

Specific Comment

While surface saturation is discussed, I think it warrants a little more attention. Many of the systems exhibit irreversible uptake that either saturates or manifests a strong coverage dependence. Many of the values quoted are initial (clean surface) uptake coefficients. To put this into perspective, an uptake coefficient of 0.01 with 1 ppb of trace gas will yield coverages near a monolayer (5 x 1014 cm-2) in only a few minutes. Perhaps the discussion in 3.3 is sufficient but I thought some more context would be useful.

Reply

The time dependence of an uptake process depends strongly on the type of interaction and varies between the extreme cases of catalytic surface reaction (no time dependence) and weak, reversible uptake with rapid surface saturation. Intermediate cases are controlled by e.g. rates of delivery of reactants to the surface. We shall add some general text to outline the importance of surface saturation.

"In many studies of trace gas uptake to surfaces evidence is obtained for surface saturation, usually observable as a decrease in the experimental uptake coefficient (γ). The rate of change of γ depends on a number of factors, depending on the type of interaction. For a purely reversible process this will depend on surface capacity and the concentration of the gas-phase species. For a reactive process it will depend on the number of reactive sites or the rate of delivery of a surface reactant as well as the gas-phase concentration of the trace-gas(es). γ may sink from near unity to near zero on time scales of minutes or hours, or, for the case of a reactive uptake with no consumption of reactive surface sites/species will be time independent and equal to the initial uptake coefficient. The frequent use in laboratory studies of very large surface to volume ratios (use of bulk substrates) to force reactions to take place on reasonable time scales can also disguise the time dependence of a process (i.e. the onset of surface saturation), which in the atmosphere may be important.

Technical corrections

Comment

Page 5247; "Equation (5) may also be used to parameterise the temperature dependence of the uptake coefficient observed at a given time or averaged over a given time interval." Do the authors mean time dependence?

Reply

No. A temperature dependence is also built into expression (5) as B is a temperature dependent parameter (mainly via k_{des}).

Comment

Page 5246 and 5249, eqn. 3, eqn. 11 and maybe some of the others should be formatted like eqn. 13 so that numerator and denominator are clearly defined.

Reply

Agreed. Equations 3, 10 and 11 will be re-formatted using horizontal dividing lines for numerator and denominator.

Comment

I don't understand the symbol "=c" for thermal velocity. It is very confusing in the context of some of the equations. Maybe this is an html formatting issue.

Reply

This was indeed a formatting problem, which will be resolved in revision.

Comment

The discussion of units in 3.4 is a little confusing. Page 5248, eqn. 6 is given in terms of the fractional coverage (unitless) but the discussion of the use of eqn. 6 and the subsequent discussion of the linear regime partition coefficients is in terms of surface coverage (# cm-2). It is not until eqn. 15 that θ is defined (as N/Nmax). Perhaps that should be made explicit in eqn. 6.

Reply

Eqn 6 will be modified to include the equality of θ *to* N / N_{max}. We shall also add the term N_{max} and N to Table 1.

Comment

I don't think there should be a factor of "k_{BT}" in the "K_{linP}" term of eqn. 13. As it is rendered, the term is not unitless.

Reply

Agreed, this equation will be corrected in the revised version.

Comment

Table on page 5250 is missing right parenthesis on some partition coefficients in the "To" column. Also a superscript "a" appears on the "T" in the third row and I am not sure why.

Reply

The missing parentheses will be added in revision. The superscript "a" referred to a missing footnote " [a] Note that in some cases a pressure "referenced to STP (1 atm)" is reported. In this case the multiplication factor is 3.717×10^{-20}, independent of temperature."

Comment

What is "[X]" in eqn. 15? Should this be "[X]g"? Also, this notation seems to take different forms (e.g. " [Xg]" appears in eqn. 13, the only place it is used).

Reply

[X] should indeed be $[X]_g$. This will be amended in revision. We shall also clean up mixed usage of $[X_g]$ and $[X]_g$.

Comment

I assume notation like "KLangC(X)", in eqn. 16, and "γ_{gs}(X)", in eqn. 17, refer to parameters for species "X" but this should be made explicit.

Reply

Correct. This will be clarified in the text.

Comment

I didn't understand this from page 5253; "Equation (16) demonstrates that γ 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)." Do they mean at high pressures of X? Similarly, for the next sentence; "This is especially important when interpreting data from laboratory experiments performed using gas-phase reactant concentrations, which lead to significant surface coverage." Do they mean "high gas-phase reactant concentrations"?

Reply

No. Only if the coverage (defined by KLanc * [X]g) is large does γ depend on [X]. High gas pressures do not necessarily lead to large coverages (e.g. if K_{LangC} is small).

Comment

It may be useful to point out that, in practice, it is very difficult to experimentally differentiate between LH and ER surface mechanisms. The uptake must be evaluated in the high pressure/high coverage regime for both reactants and the data must be of high quality.

Reply

True. We shall add a line of text stating exactly this in section 3.5

Comment

On page 5255, they may want to describe eqn. 21 as; "For trace gas reactive uptake to the bulk..." to distinguish from eqn. 20.

Reply

Agreed. Correction will be made in revision.

Comment

On page 5256, in eqn 23, I presume "r" is the drop radius. That should be defined.

Reply

Correct. This will be defined in the revised manuscript.

Comment

Also on page 5256, I am not sure about the validity of eqn. 24. The text implies that it is the effective Henry's law constant for an acid but the formula is not right (it implies that solubility is enhanced in acidic solutions). If the equation is explicitly for an acidic species, then that should be made clear.

Reply

The equation is for acidic species. This will be made clear: "Note that for an acidic species that can dissociate………etc"

Comment

On page 5256. There are two Hanson et al. 1994 references. Please indicate which is which.

Reply

One reference is Hanson et al 1994, the other is Hanson and Ravishankara, 1994.

Comment

On page 5257, there is no Hu 1995 reference.

Reply

The Hu reference is correctly titled, but has an incorrect journal year and page numbers (should be J. Phys. Chem. 99, 8768-8776, 1995.). This will be corrected in revision.

Comment

In datasheet, V.A2.4, the γ value maybe should be “10-6”

Reply

The comment presumably refers to the preferred value of γ. This indeed should be 10^{-6} and not 10^{6}. This will be corrected in revision.

Comment

On page 5489, footnote (c), should maybe be “0.25 m2” for surface area.

Reply

Yes, this will be corrected in revision.

Comment

There is no appendix 3.

Reply

The lack of Appendix 3 is related to a requirement to keep the datasheet numbering on the IUPAC web-site and the publications in ACP consistent. An Appendix 3 with text to explain the situation will be added to the revised manuscript. This was discussed with the editorial office.