

## ***Interactive comment on “Compilation of Henry’s law constants, version 3.99” by R. Sander***

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### **Reply to referees**

I thank both referees for their useful suggestions how to improve the manuscript. Specific replies are embedded below. The changes made to the manuscript are highlighted in the attached file.

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## Referee #1

*In Table 6 (where the Henry's law values are summarized), the \*Note\* needs to include more details, e.g. whether the reported value represents physical solubility or the effective Henry's law that includes certain equilibrium, whether the value is for pure water, salt solution, sea water, aqueous aerosol, etc.*

I have now mentioned that the Henry's law constants refer to pure water as solvent unless noted otherwise. See below for my reply regarding effective Henry's law constants.

*For the author's reference, Sander et al (JPL 2011) compiles pure water Henry's law constants for 120 species accompanied with 93 notes, while this work summarizes >3000 species but only followed by 300 notes.*

The NASA Panel for Data Evaluation provides recommendations for  $\approx 120$  species based on available literature values (JPL 2011). The reasons for the choices are explained in their notes. Unfortunately, providing recommendations for the  $> 3000$  species in my list is far beyond the scope of this work for a single author (note that the NASA panel has 12 members). What I do provide though, are detailed information how the numbers in the original publication were converted into a uniform format ( $\text{mol m}^{-3} \text{Pa}^{-1}$ ) and how the temperature dependence was calculated by linear regression. This information can be found in the Fortran90 code in the supplement, as explained in section 4.

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*some compounds of great atmospheric interests are missing in the list, e.g. epoxide compounds formed from isoprene oxidation. Isoprene has large global source and potential contribution to SOA formation, and the recently identified epoxide compounds are key intermediates to the isoprene SOA formation. These compounds are expected to be highly water-soluble and Henry's law constant estimated to be on the order of  $10^8$ - $10^9$  M/atm (EPI suite by Chan et al 2010). Also epoxide formed from toluene oxidation (e.g. 2,3-epoxy-6-oxo-heptanal, 20% yield) its Henry's law constant is estimated to be on the order of  $10^5$  M/atm (SPARC estimated by McNeill 2012). Given this work is reviewed by a journal in the field of atmospheric science, I recommend that the author include these compounds.*

Thanks for mentioning these publications, I was not aware of them. 2,3-epoxy-2-methyl-1,4-butanediol (IEPOX) and 2,3-epoxy-6-oxo-heptenal (TOL\_EPOX) have now been added to the list.

*Page 29616, Line 22, "... to calculate the vaporization of chemicals from rivers and during waste water treatment" citation needed. Also mass transport may be limiting for large water bodies.*

As examples, I have added citations to Shen (1982), Hawthorne et al. (1985) and David et al. (2000).

*Page 29619, Line 18, Equation (2) "...where  $R$  = gas constant" please remind the readers the  $R$  value and units associated with this formulation.*

The value and units of  $R$  are already shown in Table 4. In the explanation of Equation (2), I now refer to Table 4.

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Page 29620, Line 11, "There are some advantages to describe... molality" the advantages are not discussed until the next page.

The text has been rearranged. The advantages are now described earlier.

Page 29623, Line 13, Equation (16) Please specify the Henry's law constant  $H$  here follows which definition(s).

In Equation (16), I use the generic symbol  $H$  on purpose because this equation is valid for all variants of the Henry's law solubility constants.

Page 29624, Section 2.7. In addition to the "salting out" effect, there is also "salting in" effect. This section needs to be expanded in light of this. [...] Also, a few more refs may be of atmospheric interest: Kampf et al 2013, Kurtén et al 2014.

I have added the "salting in" effect to Section 2.7, citing the work of Kampf et al. (2013) and Kurtén et al. (2014).

Page 29613, Section 3.2.4. I recommend clarify which citation is for what compound, and could include this information in Table 6 for each individual compounds, or make another table.

As suggested, I have added the compounds to all references in Section 3.2.4. In Table 6, there are notes already for values referring to sea water.

Page 29726-29731, NOCl, ClNO<sub>2</sub>, BrNO<sub>2</sub>, HI, HOI, SO<sub>2</sub> sections (and perhaps others too), please include values or estimates in the table. For those commonly assumed to be with infinite effective Henry's law constant, please include an infinite symbol in the table.

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For NOCl, ClNO<sub>3</sub>, BrNO<sub>3</sub>, HOI, SO<sub>3</sub> and several other species, I have now included the lower limits, upper limits, and infinite effective Henry's law constants into the table.

For HI, the intrinsic Henry's law constant is not available. Only the product of  $H$  and the acidity constant is known, as explained in the note.

| *Note 42: if incorrect, why not just delete it?*

During my literature study, I found many articles using and citing incorrect values, probably because the authors were not aware of an erratum. Therefore, I decided to keep these in my list to warn potential users.

| *For example, in general I find formaldehyde is well documented in this work (e.g. sufficient details are given in notes) but glyoxal is not. [...] Page 29927, glyoxal section: all effective Henry's law constant. Ip et al (2009) pure water, Zhou and Mopper (1990) sea water, Kroll et al (2005) aqueous aerosol (ammonium sulfate/sulfuric acid).*

I have added notes to all glyoxal values explaining that they are effective Henry's law constants and mentioning the composition of the aqueous phase if it is not pure water.

| *Page 30502, Line 7 "The value is probably wrong." this is rather ambiguous and lack of explanation*

I have assigned Type="W" to wrong values and added a more detailed individual explanation in a note.

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Page 30508, Line 2, Note 92 "Hedgecock et al 2005 refer to Schroeder and Munthe 1998 as the source but this value cannot be found there". Not really. In Schroeder and Munthe (1998) the authors listed Henry's law coefficients ( $\text{Pa m}^3 \text{mol}^{-1}$ ) for HgO ( $3.76\text{e-}11$  at  $25\text{degC}$ ). Also what's the point of cite Hedgecock et al here? why not directly Schroeder and Munthe or the reference(s) therein?

Thanks for noticing this! I don't know why I overlooked the value for HgO. I have now added the data from Schroeder and Munthe (1998) to the list.

Referee #2

*I find the section on the different ways that Henry's law constants are calculated to be particularly thorough. I found some other sections to be too concise.*

The possibility to define Henry's law constants in different ways can be quite confusing. Therefore, I decided to provide a detailed description about the definitions and the conversions between them. Other topics related to Henry's law constants have been discussed elaborately in the review articles mentioned in section 3.2.1. Instead of duplicating their text, I preferred to be concise and only provide suitable references.

*I don't like the use of  $kH$  for the Henry volatility symbol. I understand that the author is endeavoring to be consistent with IUPAC terminology, but in chemistry  $k$  is reserved for rate constants, while  $K$  is used for equilibrium constants. This work has the potential to set standards for notation and I can envision this value being used in equations also involving rate constants where the use of  $kH$  could be confusing since it is an equilibrium constant. Unless there are conflicts with fields outside of chemistry with using  $KH$ , I would recommend  $KH$  over  $kH$  for the volatility symbol.*

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I fully agree that the lower case letter  $k$  for the Henry volatility symbol can be confusing as it is also used for rate constants. Indeed, my only reason for using  $k_H$  was to follow the IUPAC recommendations. I don't know why IUPAC chose the lower case letter; it is not explained in their "Green Book". I now agree that using the upper case letter  $K$  is a better choice even though this is not consistent with the IUPAC recommendations. I have switched the whole text to the symbol  $K_H$  now. The revised section 2.3 explains the reasons for not following the IUPAC recommendations.

*Table 6: Can the author explain why all values have two significant figures, especially for when the original measurements may have had the precision to merit additional significant figures? This might be best addressed in the supplemental information unless the explanation is short.*

It was my aim to bring all Henry's law data from a wide range of definitions into a uniform format, and I chose to show two significant figures for all data. Indeed, there are a few cases where more (or less) digits would have been justified. However, deciding upon the number of significant digits would require a detailed analysis of the original work, and in many cases these publications don't even contain the necessary information.

*Line 20, page 29619: Can the author provide a brief (1-2 sentence) overview of Ostwald coefficients?*

According to Battino (1984), Ostwald coefficients can be defined either using the volume of the solvent or the volume of the solution in the definition. Also, the extrapolation to zero concentration can be done either assuming ideality or taking non-ideality into account. For dilute solutions, these differences in the definitions are small compared to experimental uncertainties of measured Henry's law constants.

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| *Line 10, page 29622: Does the author have a reference for KAW ?*

It seems that the symbol  $K_{AW}$  is mainly used in chemical engineering. Examples for articles that use this symbol are: van Roon et al. (2005), Paasivirta and Sinkkonen (2009), Li et al. (2007), Ma et al. (2010), and Xu and Kropscott (2014).

| *Line 15, page 29625 and following paragraph: Upon reading the conclusion, it became clear that this paper is to be the peer-reviewed reference for the online database henrys-law.org. However, out of that context this paragraph is confusing. I recommend an explanation in this paragraph of the online database.*

I have restructured section 3.1 in order to explain better that this paper is meant as a peer-reviewed reference for the online database. Please note that the abstract also mentions the availability of the compilation at henrys-law.org.

| *Even in the context of understanding the database and that this is the reference, several points are unclear. Why was it necessary to recalculate values and how were they recalculated?*

The tabulated values in version 3 from 1999 were obtained with a pocket calculator and miscellaneous software tools. For version 4, the whole system was ported to Fortran90. Minor differences between the versions can have several reasons, e.g., using a different number of significant digits for conversion factors, or making a different choice of outliers for regression analysis.

| *I am unfamiliar with the term "grey literature".*

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According to wikipedia, grey literature is “defined as academic literature that is not formally published” ([https://en.wikipedia.org/wiki/Grey\\_literature](https://en.wikipedia.org/wiki/Grey_literature)).

*Line 22, page 29625 and following paragraph: The description of the sorting order requires elaboration. It is currently unclear where to locate compounds containing multiple elements - e.g. does NO<sub>2</sub> appear in the N section or the O section?*

The order chosen is: O, H, N, F, Cl, Br, I, S, rare gases, others. Compounds with several of these elements are put into the last of the applicable sections. For example, nitryl chloride which contains O, N and Cl, is listed in the Cl section.

*Line 3, page 29630 and following paragraph: This section seems too brief since it has the potential to be quite useful to people making Henry's law measurements. If the review articles have a theme (e.g. inorganic gas solubility in sea water), could the author indicate that in the review list? Line 10, page 20630: If these papers contain one way of measuring (or calculating) Henry's law values, can that briefly be listed next to the citation?*

The review articles mentioned in the first paragraph of section 3.2.1 are quite generic, they don't focus on a special theme. For the references to experimental methods papers, I have now added the presented method in brackets.

*Line 6, page 29630: Is there any practical guidance from Smith and Harvey (2007) that is worth repeating here?*

Smith and Harvey (2007) provide suggestions how to avoid common pitfalls when using Henry's law constants in chemical engineering. The 3 main topics are: 1) Extrapolating

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over large temperature intervals, 2) Pitfalls with chemically reacting systems, and 3) Pitfalls with units. These topics are covered in my manuscript in sections 2.6, 2.7 and 2.4, respectively. Note that these section numbers refer to the revised manuscript.

*Line 2, page 29625: The section on Setschenow constants is extremely brief. Can the author provide examples of how Setschenow parameters are defined, and explain why molality is preferred?*

The reason why molality is preferred has been presented by Sander (1999): “Adding dry salt to a solution does not change the molality of other solutes since the molality refers to the mass of the *solvent*, not the mass of the *solution*. In contrast, adding salt to a solution increases its volume and thus decreases the concentrations of its other solutes.” Thus, a non-zero concentration-based Sechenov coefficient would be obtained even without degassing of the solution. A definition of the molality-based Sechenov constant has been added to the manuscript.

*Section 3.2.4: The author is missing several references, including the original reference to Setschenow constants: [...] Additional references on salting constants (in addition to those mentioned by Reviewer 1) include: [...]*

Thanks for mentioning these references to me. I have added them to the manuscript, and also mention the chemical compounds that they refer to.

*Line 6, page 29624: change "ways" to "methods"*

Done.

| *Line 11, page 29625: change "(about 20. . .25C and 1 atm)" to "(between 20 and 25C and 1 atm)"*

Done.

| *Line 23, page 29625: The term "organic" typically refer to those that contain C and H (and heteroatoms if applicable). I suggest changing "organic substances" to "carbon-containing compounds".*

Done.

| *Line 22, page 29626: I think that CO and CO2 are likely to be species of very high interest and would thus merit their own listings in this section.*

A new entry "Carbon oxides" has been added.

| *Line 23, page 29629: You could say this more concisely as "The table in the online version of this document has been hyperlinked to the appropriate notes, and to NIST Chemistry WebBook from the CAS numbers.*

I changed the sentence to: "The table in the pdf of this document has been hyperlinked to the appropriate notes, and to the NIST Chemistry WebBook from the CAS numbers." Note that I prefer "pdf" instead of "online version" because the links to the notes also work when viewing the pdf offline.

| *It should be Setschenow constants, rather than Setschenov constants.*

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Unfortunately, there are different transliterations of the cyrillic name into English and German, see [https://en.wikipedia.org/wiki/Ivan\\_Sechenov](https://en.wikipedia.org/wiki/Ivan_Sechenov) and [https://de.wikipedia.org/wiki/Iwan\\_Michailowitsch\\_Setschenow](https://de.wikipedia.org/wiki/Iwan_Michailowitsch_Setschenow). I have now mentioned both names in the text.

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Please also note the supplement to this comment:

<http://www.atmos-chem-phys-discuss.net/14/C12135/2015/acpd-14-C12135-2015-supplement.pdf>

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Interactive comment on Atmos. Chem. Phys. Discuss., 14, 29615, 2014.

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