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.

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 speces but only followed by 300 notes.*

The NASA Panel for Data Evaluation provides recommendations for ≈ 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 ($\mathrm{mol\,m^{-3}\,Pa^{-1}}$) 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.

> *some compounds of great atmospheric interests are missing in the list, e.g. expoxide 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 rives 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.

> *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 defination(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" effecti, 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 interesests: Kampf et al 2013, Kurten 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 refering to sea water.

> *Page 29726-29731, NOCl, ClNO3, BrNO3, HI, HOI, SO3 sections (and perhaps others too), please include values or estimates in the table. For those commenly assumed to be with infinite effective Henry's law constant, please include an infinite symbol in the table.*

For NOCl, $ClNO_3$, $BrNO_3$, HOI, SO_3 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.

> *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 (Pa m3 mol-1) for HgO (3.76e-11 at 25degC). 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 prefered 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.*

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.

> *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".*

According to wikipedia, grey literature is "defined as academic literature that is not formally published" (`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 NO2 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 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.*

Unfortunately, there are different transliterations of the cyrillic name into English and German, see `https://en.wikipedia.org/wiki/Ivan_Sechenov` and `https://de.wikipedia.org/wiki/Iwan_Michailowitsch_Setschenow`. I have now mentioned both names in the text.

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Compilation of Henry's law constants for water as solvent, version 3.99e

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Abstract. Many atmospheric chemicals occur in the gas phase as well as in liquid cloud droplets and aerosol particles. Therefore, it is necessary to understand the distribution between the phases. According to Henry's law, the equilibrium ratio between the abundances in the gas phase and in the aqueous phase is constant for a dilute solution. Henry's law constants of trace gases of potential importance in environmental chemistry have been collected and converted into a uniform format. The compilation contains 17092 values of Henry's law constants for 4628 species, collected from 672 references. It is also available on the internet at http://www.henrys-law.org.

1 Introduction

Henry's law is named after the English chemist William Henry, who studied the topic in the early 19th century. In his publication about the quantity of gases absorbed by water (Henry, 1803), he described the results of his experiments:

> "[...] water takes up, of gas condensed by one, two, or more additional atmospheres, a quantity which, ordinarily compressed, would be equal to twice, thrice, &c. the volume absorbed under the common pressure of the atmosphere."

In other words, the amount of dissolved gas is proportional to its partial pressure in the gas phase. The proportionality factor is called the Henry's law constant. In atmospheric chemistry, these constants are needed to describe the distribution of trace species between the air and liquid cloud droplets or aerosol particles. In another area of environmental research, the constants are needed to calculate the vaporization of chemicals from rivers and during waste water treatment (e.g. Shen, 1982; Hawthorne et al., 1985; David et al., 2000).

Section 2 provides theoretical background about Henry's law and commonly used quantities and units. In Sect. 3, the compilation of Henry's law constants is described in detail. Additional information can be found in the electronic supplement, which is described in Sect. 4.

2 Theoretical background

This publication tries to follow the recommendations of the International Union of Pure and Applied Chemistry (IUPAC) as far as possible. General recommendations for physical chemistry have been published in the so-called "Green Book" by Mills et al. (1993). In addition, there are also the more specific articles about atmospheric chemistry by Calvert (1990) and about solubility by ~~and~~ Gamsjäger et al. (2008, 2010). In accordance with the Green Book, the name "Henry's law constant" is used here throughout the text, not "Henry's law coefficient". IUPAC recommendations for terminology, symbols, and units of Henry's law constants are described in the following sections.

2.1 Fundamental types of Henry's law constants

There are many variants of Henry's law constants which can all be classified into two fundamental types: One possibility is to put the aqueous phase into the numerator and the gas phase into the denominator, i.e., define the constant as the quotient A/G. Here, A and G are quantities describing the equilibrium composition (at infinite dilution) of the aqueous phase and the gas phase, respectively. Alternatively, the Henry's law constant can be defined as the quotient G/A, which results in the inverse value. There is no advantage or disadvantage in using one or the other, the two types exist purely for historical reasons. Unfortunately, the name "Henry's law constant" is used for both types. Therefore, statements like "a large Henry's law constant" are meaningless unless the type is specified. Especially the dimensionless constants (see Sects. 2.4.2 and 2.5.3) are very error-prone because their type cannot be deduced from the unit. In order to have a consistent terminology, I recommend the name "Henry's law solubility constant" (or "Henry solubility" for conciseness) when refering to A/G. When refering to G/A, the name "Henry's law volatility constant" (or "Henry volatility") is used.

2.2 Variants of Henry's law constants

For both of the fundamental types described in the previous section, there are several variants. This results from the multiplicity of quantities that can be chosen to describe the composition of the two phases. Typical choices for the aqueous phase are molar concentration (c_a), molality (b), and molar mixing ratio (x). For the gas phase, molar concentration (c_g) and partial pressure (p) are often used. Note, however, that it is not possible to use the gas-phase mixing ratio (y). At a given gas-phase mixing ratio, the aqueous-phase concentration c_a depends on the total pressure and thus the ratio y/c_a is not a constant.

There are numerous combinations of these quantities. The most frequently used variants of Henry solubilities and Henry volatilities are presented in Sects. 2.4 and 2.5, respectively. Conversion factors between them are shown in ~~Tabs.~~Tables **??**, **??**, and **??**. More detailed information about the conversion between different units and definitions of Henry's law constants can be found in Sander (1999) or Sazonov and Shaw (2006).

2.3 Symbols

In the current literature, a plethora of different symbols is used for the Henry's law constants. Several symbols are used for the same variant, and sometimes the same symbol is used for different variants. However, for this work a consistent terminology is indispensable. For Henry's law solubility constants, I follow the IUPAC recommendation for atmospheric chemistry by Calvert (1990) and use the symbol H. ~~For~~ Choosing a suitable symbol for Henry's law volatility constants ~~, the symbol k_H is used as recommended in~~ is more difficult. Although the IUPAC Green Book by Mills et al. (1993) recommends the symbol k_H with a lower case letter k, this symbol is hardly used in the literature at all. A major disadvantage is the internal inconsistency with other IUPAC recommendations: Normally, the lower case letter k describes rate constants, whereas the upper case letter K describes equilibrium constants (Mills et al., 1993). Considering this problem, I decided to use and recommend the symbol K_H with an upper case letter K.

To specify the exact variant of the Henry's law constant, two superscripts are used. They refer to the numerator and the denominator of the definition. For example, H^{cp} refers to the Henry solubility defined as c/p.

If H refers to standard conditions (~~$T^\ominus = 298.15$~~ $T^\ominus = 298.15$ K) it will be denoted as $H^\ominus$.

A summary of the symbols is shown in ~~Tab.~~Table **??**.

2.4 Henry's law solubility constants H

2.4.1 Henry solubility defined via concentration (H^{cp})

Atmospheric chemists often define the Henry solubility as:

$$H^{cp} \stackrel{\text{def}}{=} c_\mathrm{a}/p. \tag{1}$$

Here, c_a is the concentration of a species in the aqueous phase and p is the partial pressure of that species in the gas phase under equilibrium conditions.

The SI unit for H^{cp} is $\mathrm{mol\,(m^3\,Pa)^{-1}}$. However, often the unit $\mathrm{M\,atm^{-1}}$ is used since c_a is usually expressed in M (1 M ~~=~~ = 1 $\mathrm{mol\,dm^{-3}}$) and p in atm (1 atm ~~= 101325~~ = 101 325 Pa).

2.4.2 The dimensionless Henry solubility H^{cc}

The Henry solubility can also be expressed as the dimensionless ratio between the aqueous-phase concentration c_a of a species and its gas-phase concentration c_g:

$$H^{cc} \stackrel{\text{def}}{=} c_\mathrm{a}/c_\mathrm{g} = H^{cp} \times RT, \tag{2}$$

where R ~~= gas constant~~ = gas constant (see Table **??**) and T ~~=~~ = temperature.

Sometimes, this dimensionless constant is called the "water-air partitioning coefficient" ~~K_WA~~ K_WA. It is closely related to the various, slightly different definitions of the "Ostwald coefficient" L, as discussed by Battino (1984).

2.4.3 Henry solubility defined via aqueous-phase mixing ratio (H^{xp})

Another Henry's law solubility constant is:

$$H^{xp} \stackrel{\text{def}}{=} x/p. \tag{3}$$

Here, x is the molar mixing ratio in the aqueous phase. For a dilute, aqueous solution the conversion between x and c_a is:

$$c_\mathrm{a} \approx x \frac{\varrho_{\mathrm{H_2O}}}{M_{\mathrm{H_2O}}}, \tag{4}$$

where $\varrho_{\mathrm{H_2O}}$ ~~=~~ = density of water and $M_{\mathrm{H_2O}}$ ~~=~~ = molar mass of water. Thus:

$$H^{xp} \approx \frac{M_{\mathrm{H_2O}}}{\varrho_{\mathrm{H_2O}}} \times H^{cp}. \tag{5}$$

The SI unit for H^{xp} is $\mathrm{Pa^{-1}}$. However, $\mathrm{atm^{-1}}$ is still frequently used.

2.4.4 Henry solubility defined via molality (H^{bp})

~~There are some advantages~~ It can be advantageous to describe the aqueous phase in terms of molality instead of concentration. The molality of a solution does not change with T since it refers to the *mass* of the solvent. In contrast, the concentration c does change with T, since the density of a solution and thus its volume are temperature-dependent. Defining the aqueous-phase composition via molality has the advantage that any temperature dependence of the Henry's law constant is a true solubility phenomenon and not introduced indirectly via a density change of the solution. Using molality, the Henry solubility can be defined as:

$$H^{bp} \stackrel{\text{def}}{=} b/p. \tag{6}$$

Here, b is used as the symbol for molality (instead of m) to avoid confusion with the symbol m for mass. The SI unit for H^{bp} is $\text{mol}\,(\text{kg}\,\text{Pa})^{-1}$. There is no simple way to calculate H^{cp} from H^{bp} since the conversion between concentration c_a and molality b involves ~~all~~ *all* solutes of a solution. For a solution with a total of n solutes with indices ~~$i = 1,\ldots,n$~~ $i = 1,\ldots,n$, the conversion is:

$$c_\text{a} = \frac{b\varrho}{1+\sum_{i=1}^{n} b_i M_i}, \tag{7}$$

where ϱ ~~=~~ = density of the solution, and M ~~=~~ = molar mass. Here, b is identical to one of the b_i in the denominator. If there is only one solute, Eq. (7) simplifies to:

$$c_\text{a} = \frac{b\varrho}{1+bM} \frac{b\varrho}{1+bM}. \tag{8}$$

Henry's law is only valid for dilute solutions where $bM \ll 1$ and $\varrho \approx \varrho_{H_2O}$. In this case the conversion reduces further to:

$$c_\text{a} \approx b\varrho_{H_2O} \tag{9}$$

and thus:

$$H^{bp} \approx H^{cp}/\varrho_{H_2O}. \tag{10}$$

~~The molality of a solution does not change with T since it refers to the massof the solvent. In contrast, the concentration c does change with T, since the density of a solution and thus its volume are temperature-dependent. Defining the aqueous-phase composition via the molality b has the advantage that any temperature dependence of H^{bp} is a true solubility phenomenon and not introduced indirectly via a density change of the solution.~~

2.5 Henry's law volatility constants ~~k_H~~ K_H

2.5.1 The Henry volatility defined via concentration (~~k_H^{pc}~~ K_H^{pc})

A common way to define a Henry volatility is dividing the partial pressure by the aqueous-phase concentration:

$$K_\text{H}^{pc} \stackrel{\text{def}}{=} p/c_\text{a} = 1/H^{cp}. \tag{11}$$

The SI unit for ~~k_H^{pc} is~~ K_H^{pc} is $\text{Pa}\,\text{m}^3\,\text{mol}^{-1}$.

2.5.2 The Henry volatility defined via aqueous-phase mixing ratio (~~k_H^{px}~~ K_H^{px})

Another Henry volatility is:

$$K_\text{H}^{px} \stackrel{\text{def}}{=} p/x = 1/H^{xp}. \tag{12}$$

The SI unit for ~~k_H^{px}~~ K_H^{px} is Pa. However, atm is still frequently used.

2.5.3 The dimensionless Henry volatility ~~k_H^{cc}~~ K_H^{cc}

The Henry volatility can also be expressed as the dimensionless ratio between the gas-phase concentration c_g of a species and its aqueous-phase concentration c_a:

$$K_\text{H}^{cc} \stackrel{\text{def}}{=} c_\text{g}/c_\text{a} = 1/H^{cc}. \tag{13}$$

~~Sometimes~~ In chemical engineering, this dimensionless constant is sometimes called the "air-water partitioning coefficient" ~~K_AW~~ K_AW.

2.5.4 The dimensionless Bunsen coefficient α

According to Sazonov and Shaw (2006), the dimensionless Bunsen coefficient α is defined as: "The volume of saturating gas, reduced to 273.15 K and 1 bar, which is absorbed by unit volume of pure solvent at the temperature of measurement and partial pressure of 1 bar". If the gas is ideal, the pressure cancels out, and the conversion to H^{cp} simply is:

$$H^{cp} = \alpha \times \frac{1}{RT^\text{STP}} \alpha \times \frac{1}{RT^\text{STP}} \tag{14}$$

with ~~T^STP =~~ T^STP = 273.15 K. Note, that according to this definition, the conversion factor is ~~not~~ *not* temperature-dependent! Independent of the temperature that the Bunsen coefficient refers to, 273.15 K is always used for the conversion. The Bunsen coefficient has been used mainly in the older literature.

2.5.5 The Kuenen coefficient S

According to Sazonov and Shaw (2006), the Kuenen coefficient S is defined as: "The volume of saturating gas, reduced to 273.15 K and 1 bar, which is dissolved by unit mass of pure solvent at the temperature of measurement and partial pressure 1 bar". If the gas is ideal, the relation to H^{cp} is:

$$H^{cp} = \sout{S \times \frac{\varrho}{RT^{\rm STP}}} \; S \times \frac{\varrho}{RT^{\rm STP}}, \tag{15}$$

where ϱ is the density of the solvent and ~~$T^{\rm STP} =$~~ $T^{\rm STP} =$ 273.15 K. The SI unit for S is $\mathrm{m^3\,kg^{-1}}$. The Kuenen coefficient has been used mainly in the older literature. IUPAC considers it to be obsolete (Gamsjäger et al., 2010).

2.6 Temperature dependence of Henry's law constants

The temperature dependence of equilibrium constants can generally be described with the van't Hoff equation (e.g. Atkins, 1986). It also applies to Henry's law constants:

$$\frac{\mathrm{d}\ln H}{\mathrm{d}(1/T)} = \sout{\frac{-\Delta_{\rm soln}H}{R}} \; \frac{-\Delta_{\rm sol}H}{R}, \tag{16}$$

where ~~$\Delta_{\rm soln}H =$~~ $\Delta_{\rm sol}H =$ enthalpy of dissolution. ~~Integrating the~~ Note that here, the letter H in the symbol $\Delta_{\rm sol}H$ refers to enthalpy and is not related to the letter H for Henry's law constants. Integrating the above equation leads to:

$$H(T) = A \times \exp\left(\frac{B}{T}\right) \tag{17}$$

with the parameters A and B. When reporting H as a function of these parameters, it is important to present sufficient significant digits of B because H depends exponentially on it. Alternatively, one can create an expression based on $H^\ominus$ at the reference temperature $T^\ominus$ ~~=~~ = 298.15 K:

$$H(T) = H^\ominus \times \exp\left(\sout{\frac{-\Delta_{\rm soln}H}{R}} \; \frac{-\Delta_{\rm sol}H}{R} \left(\frac{1}{T} - \frac{1}{T^\ominus}\right)\right). \tag{18}$$

~~Here, $H^\ominus = A \times \exp(B/T^\ominus)$ and $\Delta_{\rm soln}H/R = -B$~~

Here, $H^\ominus = A \times \exp(B/T^\ominus)$ and $\Delta_{\rm sol}H/R = -B$. In this work, the values $H^\ominus$ and ~~$\Delta_{\rm soln}H/R$~~ $\Delta_{\rm sol}H/R$ are tabulated.

The van't Hoff equation in this form is only valid for a limited temperature range in which ~~$\Delta_{\rm soln}H$~~ $\Delta_{\rm sol}H$ does not change much with temperature. To cover a larger temperature range, in which ~~$\Delta_{\rm soln}H$~~ $\Delta_{\rm sol}H$ cannot be considered constant anymore, different empirical ~~ways~~ methods can be used. Often, the temperature dependence $\mathrm{d}\ln H/\mathrm{d}(1/T)$ is expressed as the sum of several terms. Then, the analytical derivative is simply the sum of the derivatives of the individual terms. For example, Wilhelm et al. (1977) use the formula:

$$\ln H = A + B \times \left(\frac{T}{\rm K}\right)^{-1} + C \times \ln\left(\frac{T}{\rm K}\right) + D \times \left(\frac{T}{\rm K}\right). \tag{19}$$

Using the derivatives from ~~Tab.~~ Table **??**, the temperature dependence of this expression can be calculated as:

$$\frac{\mathrm{d}\ln H}{\mathrm{d}(1/T)} = 0 + B - C \times \left(\frac{T}{\rm K}\right) - D \times \left(\frac{T}{\rm K}\right)^2. \tag{20}$$

Note that the temperature dependences for H^{cp} and H^{cc} are different since the conversion factor between them includes the temperature:

$$\begin{aligned} H^{cp} &= H^{cc}/(RT) \\ \Leftrightarrow \ln H^{cp} &= \ln H^{cc} + \ln(1/R) + \ln(1/T) \\ \Rightarrow \frac{\mathrm{d}\ln H^{cp}}{\mathrm{d}(1/T)} &= \frac{\mathrm{d}\ln H^{cc}}{\mathrm{d}(1/T)} + \frac{\mathrm{d}\ln(1/T)}{\mathrm{d}(1/T)} \\ &= \frac{\mathrm{d}\ln H^{cc}}{\mathrm{d}(1/T)} + T. \end{aligned} \tag{21}$$

2.7 Effective Henry's law solubility constants $H_{\rm eff}$

The Henry's law constants mentioned so far do not consider any chemical equilibria in the aqueous phase. This type is called the "intrinsic" (or "physical") Henry's law constant. For example, the intrinsic Henry's law constant of methanal can be defined as:

$$H^{cp} = \frac{c(\mathrm{HCHO})}{p(\mathrm{HCHO})} \tag{22}$$

In aqueous solution, methanal is almost completely hydrated:

$$\mathrm{HCHO} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2C(OH)_2} \tag{23}$$

The total concentration of dissolved methanal is:

$$c_{\rm tot} = c(\mathrm{HCHO}) + c(\mathrm{H_2C(OH)_2}) \tag{24}$$

Taking this equilibrium into account, an effective Henry's law constant $H_{\rm eff}$ can be defined:

$$H_{\rm eff} = \frac{c_{\rm tot}}{p(\mathrm{HCHO})} = \frac{c(\mathrm{HCHO}) + c(\mathrm{H_2C(OH)_2})}{p(\mathrm{HCHO})} \tag{25}$$

For acids and bases, the effective Henry's law constant is not a useful quantity because it depends on the pH of the solution (Sander, 1999). In order to obtain a pH-independent constant, the product of the intrinsic Henry's law constant H^{cp} and the acidity constant K_A is often used for strong acids, e.g., for HCl:

$$H' = H^{cp} \times K_A = \frac{c(H^+) \times c(Cl^-)}{p(HCl)} \qquad (26)$$

Although H' is usually also called a Henry's law constant, it should be noted that it is a different quantity and it has different units than H^{cp}.

2.8 Dependence of Henry's law constants on ionic strength

Values of Henry's law constants for aqueous solutions depend on the composition of the solution. In general, the solubility of a gas decreases with increasing salinity ~~. This so-called~~ ("salting out"). However, a "salting in" effect has also been observed, e.g., for glyoxal (Kampf et al., 2013; Kurtén et al., 2014). The ionic strength effect can be described with the Sechenov ~~parameter~~(also transliterated "Setschenow") equation (Setschenow, 1889). There are many alternative ways to define ~~such a parameter. An equationbased on the molality of the solution is preferred.~~ the Sechenov equation, depending on how the aqueous-phase composition is described (based on concentration, molality, or molar fraction) and which variant of the Henry's law constants is used. Using the preferred quantity molality (see Sander (1999) for details), the equation becomes:

$$\log\left(\frac{H_0^{bp}}{H^{bp}}\right) = k_s \times b(\text{salt}) \qquad (27)$$

where H_0^{bp} = Henry's law constant in pure water, H^{bp} = Henry's law constant in the salt solution, k_s = molality-based Sechenov constant, and $b(\text{salt})$ = molality of the salt.

Since the atmosphere contains very dilute cloud droplets as well as highly concentrated aerosols, adequate values of Henry's law constants should be used. Unfortunately, Sechenov parameters are unknown for many species. A ~~short~~ list of some available data is presented in Sect. 3.2.4. ~~For more details, see .~~

3 Values of Henry's law constants

3.1 The data compilation

The ~~data compilation~~ compilation of Henry's law constants is presented in ~~Tab. ??~~Table ??, and it is also available online at http://www.henrys-law.org. It contains Henry's law constants for inorganic and organic species of potential importance in environmental chemistry. Most data were measured at ambient conditions (~~about~~ between 20 °C and 25 °C and 1 atm). Data at high temperatures are excluded or (if possible) extrapolated to $T^\ominus$ = 298.15 K. All data ~~refers~~ refer to aqueous solutions; octanol and other solvents are not included. ~~Most~~ The constants refer to pure water as solvent ~~, however, some data for sea water are also included.~~

~~The current compilation is based on version 3, which is still available at . The collection has been expanded substantially (from 2288 to constants and from 913 to species). In addition, all values have been recalculated. Due to different precision and rounding errors, the last digit of the Henry's law constants has changed in a few cases. Also, a few more publications from the grey literature could be obtained.In these cases, the original data are used now instead of those cited by others.In a few cases, this also resulted in slightly different values~~unless noted otherwise (e.g., sea water).

Inorganic substances are sorted according to the elements they contain. The order chosen is: O, H, N, F, Cl, Br, I, S, rare gases, others. ~~Organic substances (i.e.everything with carbon,~~ 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. Carbon-containing compounds (including CO and CO_2) are sorted somewhat arbitrarily by increasing chain length and complexity. Hetero atoms (O, N, F, Cl, Br, I, ~~and~~ S, P, etc.) are sorted in the same order as for inorganic compounds. The table contains the following groups of species:

The first column of the table shows the systematic name, the chemical formula, trivial names (if any), and the CAS registry number (in square brackets).

The column labeled ~~'~~"H^{cp}~~'~~" contains the Henry's law solubility constants as defined in Eq. (1), rounded to two significant digits and given in the unit $\text{mol}/(\text{m}^3\,\text{Pa})$.

The column labeled ~~'~~"$\mathrm{d}\ln H/\mathrm{d}(1/T)$~~'~~" contains the temperature dependence of the Henry solubility as defined in Eq. (18), rounded to two significant digits and given in the unit K. If the term ~~$\Delta_{soln}H$~~ $\Delta_{sol}H$ is temperature-dependent, the value of $\mathrm{d}\ln H/\mathrm{d}(1/T)$ is calculated at $T^\ominus$ = 298.15 K.

For each table entry the column labeled ~~'type'~~ "type" denotes how the Henry's law constant was obtained in the given reference. Literature reviews are usually most reliable, followed by original publications of experimental determinations of H. Other data has to be treated more carefully. The types listed here are roughly ordered by decreasing reliability:

"L" The cited paper is a ~~literature review.~~ *literature* review.

"M" Original publication of a ~~measured value. Vapor~~ *measured* value.

"V" *Vapor* pressure of the pure substance divided by aqueous solubility (sometimes called "VP/AS").

"R" The cited paper presents a ~~recalculation~~ *recalculation* of previously published material (e.g. extrapolation to a different temperature or concentration range). ~~Thermodynamical calculation ($\Delta_{\text{soln}}G = -RT\ln H$~~

"T" *Thermodynamical* calculation ($\Delta_{\text{sol}}G = -RT\ln H$, see Sander (1999) for details).

"X" The original paper was not available for this study. The data listed here was found in a secondary source.

"C" The paper is a ~~citation~~ *citation* of a reference which I could not obtain (e.g. personal communication, Ph.D. theses, internal papers etc.).

"Q" The value is an estimate obtained with the "~~quantitative~~ *quantitative* structure property relationship" (QSPR) method, see Staudinger and Roberts (1996) for details~~).~~ .

"E" The value is an ~~estimate~~*estimate*. Estimates are only listed if no reliable measurements are available for that compound.

"?" The cited paper doesn't clearly state how the value was obtained.

"W" The value is probably wrong.

In some cases there might be good agreement between different authors. However, if the original work they refer to is not known one has to be careful when evaluating the reliability. It is possible that they were recalculating data from the same source. The similarity in that case would not be due to independent investigations. 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.

~~When viewing this pdf online, it is possible to click on the CAS registry number to open the web page about this species from the NIST Chemistry WebBook~~The version number of the current compilation is 3.99e. Based upon version 3 (still available at http://www.henrys-law.org), the list has been expanded substantially (from 2288 to 17092 constants and from 913 to 4628 species). In addition, all values have been recalculated using a system of Fortran90 modules. Due to different precision and rounding errors, the last digit of the Henry's law constants has changed in a few cases. Also, a ~~click on the number of a note in the table will lead you to the corresponding note~~few more articles could be obtained from the grey literature (academic publications not formally published). In these cases, the original data are used now instead of those cited by others. In a few cases, this also resulted in slightly different values.

3.2 Further sources of information

3.2.1 Review articles

Several reviews about Henry's law have been published, starting with Markham and Kobe (1941), up to more recent publications such as Wilhelm et al. (1977), Mackay and Shiu (1981), Staudinger and Roberts (1996), Staudinger and Roberts (2001), Fogg and Sangster (2003), and Sander et al. (2011). Practical guidance on the use of Henry's law has been published by Smith and Harvey (2007).

Experimental methods to obtain Henry's law constants as well as indirect (theoretical) methods have been described and compared by ~~various authors~~several authors. Only a brief summary of some articles is given here. For details, the reader is referred to the original publications: Battino and Clever (1966) [miscellaneous methods, partially of historical interest], ~~including~~ Betterton (1992) [head-space method, bubble column method, thermodynamic cycles, calculation from vapor pressure and solubility, linear correlations], ~~,~~ Turner et al. (1996) [static methods, mechanical recirculation methods, separate measurement of solubility and pure species vapor pressure, ebulliometry, perturbation chromatography], Staudinger and Roberts (1996) [batch air stripping, concurrent flow technique, Equilibrium Partitioning in Closed Systems (EPICS), calculation via Quantitative Property Property Relationships (QPPR), Quantitative Structure Property Relationships (QSPR), UNIversal quasichemical Functional group Activity Coefficients (UNIFAC)], Brennan et al. (1998) ~~,~~ [comparison of predictive methods], Sander (1999) ~~, and~~ [QPPR, QSPR, thermodynamic calculations], and Fogg and Sangster (2003) ~~.~~ [miscellaneous methods].

3.2.2 Internet

On the internet, the following pages provide Henry's law constants:

- The NIST Chemistry WebBook at http://webbook.nist.gov/chemistry.
- The Pesticide Properties Database (PPD) at http://www.ars.usda.gov/Services/docs.htm?docid=14199.
- The Screening Information Datasets (SIDS) of the United Nations Environment Programme (UNEP) at http://www.chem.unep.ch/irptc/sids/OECDSIDS/INDEXCHEMIC.htm provide data sets including Henry's law constants for many species.
- A program to calculate Henry's law constants is available at http://www.epa.gov/opptintr/exposure/pubs/episuitedl.htm.
- Vapor-liquid equilibrium data from the "Dortmund Data Bank" at http://www.ddbst.com/en/EED/VLE/VLEindex.php.
- The GSI chemical properties database at http://www.gsi-net.com/en/publications/gsi-chemical-database.html.

- The Hazardous Substances Data Bank (HSDB), included in the toxnet database at http://toxnet.nlm.nih.gov/newtoxnet/hsdb.htm.
- Effective Henry's law constants calculated by Hodzic et al. (2014) are available at https://www2.acd.ucar.edu/modeling/gecko.

3.2.3 QSPR

Several publications apply the "Quantitative structure property relationship" (QSPR) method to obtain theoretical predictions for Henry's law constants: Pierotti et al. (1959), Deno and Berkheimer (1960), Nirmalakhandan and Speece (1988b), Dunnivant and Elzerman (1988), Brunner et al. (1990), Sukuzi et al. (1992), Russell et al. (1992), Sukuzi et al. (1992), Brennan et al. (1998), English and Carroll (2001), Dearden and Schüürmann (2003), Yaffe et al. (2003), Kühne et al. (2005), Modarresi et al. (2007), Raventos-Duran et al. (2010).

3.2.4 Salt solutions

Some information about Henry's law constants for salt solutions (Sechenov ~~coefficients~~constants, see Sect. 2.8) can be found in these publications: McDevit and Long (1952) [benzene], Gordon and Thorne (1967a) and Gordon and Thorne (1967b) [naphthalene], Meadows and Spedding (1974) [CO], Zafiriou and McFarland (1980) [NO], Przyjazny et al. (1983) ~~, ~~[organic sulfur compounds], Hunter-Smith et al. (1983) [halocarbons], Almeida et al. (1983) [naphthols], Sanemasa et al. (1984) [benzene, alkylbenzenes], Dacey et al. (1984) [dimethyl sulfide], Wisegarver and Cline (1985) [chlorofluorocarbons], Johnson and Harrison (1986) ~~, ~~[OCS], Zhou and Mopper (1990) [aldehydes, ketones], Kames and Schurath (1992) ~~, ~~[organic nitrates], Benkelberg et al. (1995) [propanone, ethanal, ethane nitrile], De Bruyn et al. (1995b) ~~, ~~[organic sulfur compounds], Moore et al. (1995) ~~, ~~[halogenated methanes], Dewulf et al. (1995) [halocarbons, aromatics], Wong and Wang (1997) ~~, ~~[dimethyl sulfide], Xie et al. (1997) [organic compounds], ~~, ~~Peng and Wan (1998) [halocarbons, aromatics], Moore (2000) [halocarbons], Ni et al. (2000) [organic compounds], Bullock and Teja (2003) ~~, ~~[methanol], Endo et al. (2012) [alkanals, alkanones, nitroalkanes, alkylbenzenes, fluorinated alcohols, additional compounds with various polar functional groups], Yu and Yu (2013) [theoretical predictions], and Wang et al. (2014) [38 organic compounds].

4 The electronic supplement

The ~~electronic supplement, available at , ~~Supplement contains several files with additional information about the compiled Henry's law constants. It includes a README file with a detailed description. Here, only a short summary is given:

- The files henry_*.f90 are the Fortran 90 code that was used to convert the values from the original publications to the uniform format with the unit $\mathrm{mol/(m^3\,Pa)}$. The code and the comments in the code can be used to double-check that the conversion was done correctly.
- If the original publications contained measurements at different temperatures, the fortran code often contains all individual data points, not just the regression line that was used to show the temperature dependence in ~~Tab.~~Table ??. In addition, the supplement contains plots showing the data points as well as the regression lines according to Eq. (18).
- If the Henry's law constants are needed in electronic form, it is cumbersome to extract them from the pdf of this article. Therefore, the supplement contains declarations of the Henry's law constants (H^{cp}, H^{cc}, H^{xp}, H^{bp}, ~~k_{H}^{pc}, k_{H}^{px}, k_{H}^{cc}~~K_{H}^{pc}, K_{H}^{px}, K_{H}^{cc}, and α) in Fortran 90 syntax.

5 Summary and outlook

A comprehensive compilation of Henry's law constants has been presented. The collection, which is also available at http://www.henrys-law.org, will be continously maintained, updated and extended in the future. If necessary, errata will also be posted on this web page. In addition to providing a source of information, I hope that this work will help to identify gaps in our current knowledge and stimulate research projects. In particular, it seems that even for some well-known chemicals like HCl, Br_2, and BrCl, there is a large uncertainty in the value of the Henry's law constants. I always welcome information about new measurements of Henry's law constants to be included in the table.

The Supplement related to this article is available online at doi:10.5194/acp-0-1-2015-supplement.

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Staffelbach, J. Staudinger, J. St-Pierre, G. Tyndall, J. Überfeld, C. Verlinde, R. Vogt, P. Warneck, and J. C. Wheeler. The CAS registry number is a registered trademark of the American Chemical Society. The service charges for this open access publication have been covered by the Max Planck Society.