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Henry's law constants

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Abstract: Henry's law states that the abundance of a volatile solute dissolved in a liquid is proportional to its abundance in the gas phase. It applies at equilibrium and in the limit of infinite dilution of the solute. For historical reasons, numerous different definitions, names, and symbols are used in the literature to express the proportionality coefficient, denoted the "Henry's law constant". Here, a consistent set of recommendations is presented. An important distinction is made between two new recommended reciprocal quantities "Henry's law solubility constant" (H_s) and "Henry's law volatility constant" (H_v). Eight recommended variants of H_s and H_v are described and relations among them presented.

Keywords: Henry's law; solubility; volatility; gas-solution equilibrium

1 Introduction

In his original publication from 1803, William Henry described his discovery [1]:

"[. . .] 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."

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Today, this proportionality, at equilibrium, between the abundance of a species in the gas phase and its abundance in a liquid solution is known as Henry's law. It is a limiting law, analogous to the ideal gas law, valid only in the limits of infinite dilution of the solute and ideality in the gas phase. Departure from ideality can be accounted for in Henry's law by replacing abundances by activities (see Sect. 4.3).

Since the Henry's law constant is an extrapolation to infinite dilution, it cannot be measured directly in a laboratory. To distinguish these, we suggest the name "experimental Henry's law constant" for values obtained at a non-zero abundance of the solute.

Values of Henry's law constants are known for many chemical species, mainly for aqueous solutions but also for other solvents. Numerous different and sometimes inconsistent definitions, names, and symbols for the Henry's law constant are currently used in the scientific literature as illustrated in the detailed survey in the supplement.

Unfortunately, there is also a large variety of symbols used in IUPAC publications. In 1983, IUPAC recommended the symbol $\alpha_{x,B}^{\infty}$ [2, p. 571]. In the glossary of atmospheric chemistry terms (IUPAC recommendations 1990) [3], a different definition was used, and the symbol was changed to H . The IUPAC book "Chemicals in the Atmosphere: Solubility, Sources and Reactivity" from 2003 [4] contains several different symbols (\tilde{H}_x , \tilde{K}_{H_x} , K_{WA} , K_{AW} , k_H , and c_w/c_g) in different chapters. The symbol K_H (with an upper case K) was used in the introduction to the IUPAC-NIST Solubility Data Series [5]. The symbol was changed to k_H (with a lower case k) in the IUPAC recommendations from 2008 [6]. At the time of writing, the online version of the Gold Book [7] contains the recommendations from 1983.

The objective of this article is to present a consistent set of recommended quantities and symbols for Henry's law constants based on IUPAC recommendations for expressing abundances in the two phases. Additionally, formulas are provided for converting between the variants of H . A complete treatment of the thermodynamics underlying Henry's law is beyond the scope of this paper that focuses on quantities and symbols for the Henry's law constant.

2 Recommendations

The multiplicity of expressions for the Henry's law constant exists because there are several quantities that are commonly used to express the (intensive) abun-

dance¹ of a chemical species. For a quantity describing the abundance of a species in the gas phase (generalized as Q_g here), partial pressure p and amount concentration c are commonly used. For a quantity describing the abundance of a solute in a liquid (generalized as Q_l here), choices include amount concentration c , molality b , amount fraction x and mass fraction w (Tab. 1).

The Henry's law constant H is a proportionality coefficient describing the distribution between these phases. It can be defined either as the ratio Q_l/Q_g (related to solubility) or its inverse Q_g/Q_l (related to volatility). Both choices are in common use, and the resulting Henry's law constants are reciprocals of each other. There is no inherent advantage or disadvantage in using one or the other, the two expressions exist for purely historical reasons. There are several examples in other areas of science where reciprocal quantities are commonly used, e.g., resistance *vs* conductance, wavelength *vs* wavenumber, or specific volume *vs* mass density. However, it is unique and confusing that the same term "Henry's law constant" is used for both reciprocals in measurements of the distribution of a chemical species between the gas phase and a liquid solution. Thus, a statement such as "... because of its chemical structure, the species has a very high Henry's law constant..." is ambiguous. It could refer either to a very high solubility or to a very low solubility. To distinguish between the two equivalent but different expressions of Henry's law, the following recommendations are made:

- If the Henry's law constant is defined as a quotient with the liquid phase abundance Q_l in the numerator and the gas phase abundance Q_g in the denominator, the term "Henry's law solubility constant" and the symbol H_s are recommended:

$$H_s = Q_l/Q_g$$

For conciseness, "Henry solubility" may alternatively be used.

- If the Henry's law constant is defined as a quotient with the gas phase abundance Q_g in the numerator and the liquid phase abundance Q_l in the denominator, the term "Henry's law volatility constant" and the symbol H_v are recommended:

$$H_v = Q_g/Q_l$$

For conciseness, "Henry volatility" may alternatively be used.

It would thus be unambiguous to state that "... because of its chemical structure, the species has a very high Henry's law *solubility* constant...".

¹ Here, we use "abundance" as an umbrella term for all intensive quantities which describe how much of an entity is contained in a mixture, e.g., concentration, fraction, molality, or partial pressure.

Tab. 1: Quantities commonly used to define Henry’s law constants.

Quantity	Symbol	SI Unit*
Gas phase		
Partial pressure	p	Pa
Amount concentration	c	mol m ⁻³
Solution		
Amount concentration	c	mol m ⁻³
Molality	b	mol kg ⁻¹
Amount fraction	x	1
Mass fraction	w	1

*A unit of “1” denotes a dimensionless quantity.

The umbrella terms *Henry’s law solubility constant* and *Henry’s law volatility constant* can refer to different variants of H , depending on the choice to describe the abundance in each of the phases. When necessary to avoid any ambiguity, especially when referring to a numerical value for a Henry’s law constant, an additional two-letter superscript should be added to the symbols H_s and H_v to differentiate between the variants. The letters in the superscript refer to the quantities describing the numerator and the denominator of the definition. Using this notation, H_s^{cp} , for example, refers to the Henry’s law solubility constant based on c/p , whereas H_v^{pc} refers to the Henry’s law volatility constant based on p/c . The superscripts are necessary to distinguish different variants, especially those which share a common unit. For example, $H_v^{px} = 1$ Pa and $H_v^{pw} = 1$ Pa represent different values, and simply writing $H_v = 1$ Pa could refer to either of them. Another case where the superscript is necessary is in expressions that convert one variant into another, e.g.: $H_s^{cc} = H_s^{cp} \times RT$, where R is the gas constant and T is temperature.

The most frequently used variants of Henry’s law constants are shown in Fig. 1 and listed in the glossary in Sect. 2.1. In most cases, they are equally well suited to describe Henry’s law constants. However, for some purposes, individual variants of H have certain advantages or disadvantages:

- When the molar mass of the solute or solvent is not known (e.g., for polymer solutions), it is not possible to quantify the abundance of the dissolved gas in the liquid phase using the amount fraction x . Thus, neither H_s^{xp} nor H_v^{px} can be used.
- For considerations of interfacial mass transport, the dimensionless Henry’s law constants H_s^{cc} and H_v^{cc} are most convenient. As these variants are dimensionless it is essential to specify whether the Henry’s law constant is the solubility constant or the volatility constant.

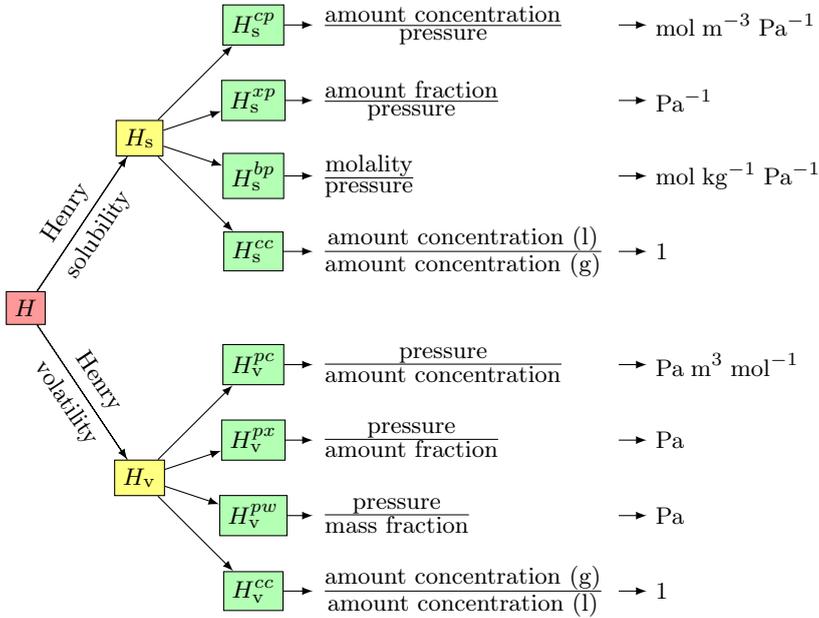


Fig. 1: Classification of Henry's law constants: recommended symbols, definitions and coherent SI units. (l) and (g) refer to the liquid phase and the gas phase, respectively. The symbol H for the umbrella term for all Henry's law constants is shown in red. The two reciprocal types (Henry solubility H_s and Henry volatility H_v) are shown in yellow, distinguished by the subscripts s and v , respectively. The recommended variants of H are shown in green, where the symbols p , c , b , x , and w in the superscript denote pressure, amount concentration, molality, amount fraction, and mass fraction, respectively. The first symbol corresponds to the numerator and the second to the denominator.

- As molality is invariant to temperature and to the addition of dry salt to the solution, using H_s^{bp} can be advantageous, in particular, in expressions involving Sechenov parameters (see Sect. 4.8).
- Because amount fraction and mass fraction are dimensionless, the Henry's law constants H_v^{px} and H_v^{pw} both have the same unit (Pa), and hence dimensional analysis cannot be used to deduce the definition. The dimensionless Henry solubility and the dimensionless Henry volatility similarly suffer from this inherent ambiguity.

It is not possible to use the amount fraction y to describe the gas phase abundance in Henry's law. At a given gas-phase amount fraction, the amount concentration c of the dissolved gas in the liquid depends on the total pressure and thus the ratio

y/c is not a constant. For the same reason, the mass fraction w cannot be used for the gas phase.

To indicate the solute that a Henry's law constant refers to, it should be put in parentheses, e.g.: The Henry's law solubility constant of ozone is $H_s(\text{O}_3)$.

The recommendations regarding Henry's law in this publication supersede those in previous IUPAC publications [3, 4, 5, 6, 7, 8, 9].

2.1 Glossary of recommended terms

2.1.1 dimensionless Henry's law solubility constant H_s^{cc} (defined via amount concentrations)

Synonym: dimensionless Henry solubility

Amount concentration of a species in the liquid phase c_l divided by the amount concentration of that species in the gas phase c_g under equilibrium conditions at infinite dilution:

$$H_s^{cc} := \lim_{c_l \rightarrow 0} \frac{c_l}{c_g}$$

Note: Instead of the amount concentrations c_l and c_g , the mass concentrations γ_l and γ_g might be used here. This yields the same dimensionless Henry solubility because the molar mass M of the solute cancels out: $\gamma_l/\gamma_g = (c_l M)/(c_g M) = c_l/c_g$. Example: The dimensionless Henry solubility of ozone in water at $T = 298.15$ K is $H_s^{cc}(\text{O}_3) = 0.25$.

Related term: Henry's law solubility constant

2.1.2 dimensionless Henry's law volatility constant H_v^{cc} (defined via amount concentrations)

Synonym: dimensionless Henry volatility

Amount concentration of a species in the gas phase c_g divided by the amount concentration of that species in the liquid phase c_l under equilibrium conditions at infinite dilution:

$$H_v^{cc} := \lim_{c_l \rightarrow 0} \frac{c_g}{c_l}$$

Note: Instead of the amount concentrations c_g and c_l , the mass concentrations γ_g and γ_l can be used here. This yields the same dimensionless Henry volatility because the molar mass M of the solute cancels out: $\gamma_g/\gamma_l = (c_g M)/(c_l M) = c_g/c_l$. Example: The dimensionless Henry volatility of ozone in water at $T = 298.15$ K is

$$H_v^{cc}(\text{O}_3) = 4.0.$$

Related term: Henry's law volatility constant

2.1.3 Henry's law

Henry's law states that at equilibrium the abundance of a volatile solute dissolved in a liquid is proportional to its abundance in the gas phase. Henry's law applies in the limit of infinite dilution of the solute. The proportionality factor is called the *Henry's law constant*. The term *Henry's law* is restricted to refer to the distribution between a solution and the gas phase. It should not be used for any other pair of phases. In particular, it should not be used to describe any liquid-liquid [10] or gas-solid (adsorption) equilibria.

Related term: Henry's law constant

Modified from [2].

2.1.4 Henry's law constant, H

Proportionality factor describing the equilibrium distribution of a chemical species between the gas phase and a liquid solution at infinite dilution of the solute according to *Henry's law*. It is an umbrella term for the reciprocal quantities *Henry's law solubility constant* and *Henry's law volatility constant*.

2.1.5 Henry's law solubility constant, H_s

Synonym: Henry solubility

Umbrella term for all variants of Henry's law constants that are defined in such a way that the numerical value increases with increasing solubility of the solute. Variants include H_s^{cp} , H_s^{xp} , H_s^{bp} , and H_s^{cc} as discussed below.

Related term: Henry's law volatility constant

2.1.6 Henry's law solubility constant (defined via amount concentration and partial pressure), H_s^{cp}

Synonym: Henry solubility (defined via amount concentration and partial pressure)

Amount concentration of a species in the liquid phase c_l divided by the partial pressure p of that species in the gas phase under equilibrium conditions at infinite

dilution:

$$H_s^{cp} := \lim_{c_1 \rightarrow 0} \frac{c_1}{p}$$

Note: The coherent SI unit for H_s^{cp} is $\text{mol m}^{-3} \text{Pa}^{-1}$. Another commonly used unit is $\text{mol} (10^{-3} \text{ m}^3)^{-1} (10^5 \text{ Pa})^{-1}$, equivalent to $\text{mol L}^{-1} \text{bar}^{-1}$.

Example: The Henry solubility of ozone in water at $T = 298.15 \text{ K}$ is $H_s^{cp}(\text{O}_3) = 1.0 \times 10^{-4} \text{ mol m}^{-3} \text{Pa}^{-1}$.

Related term: Henry's law solubility constant

2.1.7 Henry's law solubility constant (defined via liquid-phase amount fraction and partial pressure), H_s^{xp}

Synonym: Henry solubility (defined via liquid-phase amount fraction and partial pressure)

Amount fraction of a species in the liquid phase x divided by the partial pressure p of that species in the gas phase under equilibrium conditions at infinite dilution:

$$H_s^{xp} := \lim_{x \rightarrow 0} \frac{x}{p}$$

Note: The coherent SI unit for H_s^{xp} is Pa^{-1} .

Example: The Henry solubility (defined via liquid-phase amount fraction and partial pressure) of ozone in water at $T = 298.15 \text{ K}$ is $H_s^{xp}(\text{O}_3) = 1.8 \times 10^{-9} \text{ Pa}^{-1}$.

Related term: Henry's law solubility constant

2.1.8 Henry's law solubility constant (defined via molality and partial pressure), H_s^{bp}

Synonym: Henry solubility (defined via molality and partial pressure)

Molality of a species b divided by the partial pressure p of that species in the gas phase under equilibrium conditions at infinite dilution:

$$H_s^{bp} := \lim_{b \rightarrow 0} \frac{b}{p}$$

Note 1: The coherent SI unit for H_s^{bp} is $\text{mol kg}^{-1} \text{Pa}^{-1}$.

Note 2: Here, the symbol b is used for molality (instead of m) to avoid confusion with the symbol m for mass.

Example: The Henry solubility of ozone in water at $T = 298.15 \text{ K}$ is $H_s^{bp}(\text{O}_3) = 1.0 \times 10^{-7} \text{ mol kg}^{-1} \text{Pa}^{-1}$.

Related term: Henry's law solubility constant

2.1.9 Henry's law volatility constant, H_v

Synonym: Henry volatility

Umbrella term for all variants of Henry's law constants that are defined in such a way that the numerical value increases with increasing volatility of the solute. Variants include H_v^{pc} , H_v^{px} , H_v^{pw} , and H_v^{cc} as discussed below.

Related term: Henry's law solubility constant

2.1.10 Henry's law volatility constant (defined via partial pressure and amount concentration), H_v^{pc}

Synonym: Henry volatility (defined via partial pressure and amount concentration)

Partial pressure of a species in the gas phase p divided by the amount concentration of that species in the liquid phase c_1 under equilibrium conditions at infinite dilution:

$$H_v^{pc} := \lim_{c_1 \rightarrow 0} \frac{p}{c_1}$$

Note: The coherent SI unit for H_v^{pc} is $\text{Pa m}^3 \text{mol}^{-1}$.

Example: The Henry volatility of ozone in water at $T = 298.15 \text{ K}$ is $H_v^{pc}(\text{O}_3) = 1.0 \times 10^4 \text{ Pa m}^3 \text{mol}^{-1}$.

Related term: Henry's law volatility constant

2.1.11 Henry's law volatility constant (defined via partial pressure and liquid-phase amount fraction), H_v^{px}

Synonym: Henry volatility (defined via partial pressure and liquid-phase amount fraction)

Partial pressure of a species in the gas phase p divided by the amount fraction of that species in the liquid phase x under equilibrium conditions at infinite dilution:

$$H_v^{px} := \lim_{x \rightarrow 0} \frac{p}{x}$$

Note: The coherent SI unit for H_v^{px} is Pa.

Example: The Henry volatility (defined via partial pressure and liquid-phase amount fraction) of ozone in water at $T = 298.15 \text{ K}$ is $H_v^{px}(\text{O}_3) = 5.5 \times 10^8 \text{ Pa}$.

Related term: Henry's law volatility constant



2.1.12 Henry's law volatility constant (defined via partial pressure and liquid-phase mass fraction), H_V^{pw}

Synonym: Henry volatility (defined via partial pressure and liquid-phase mass fraction)

Partial pressure of a species in the gas phase p divided by the mass fraction of that species in the liquid phase w under equilibrium conditions at infinite dilution:

$$H_V^{pw} := \lim_{w \rightarrow 0} \frac{p}{w}$$

Note: The coherent SI unit for H_V^{pw} is Pa.

Example: The Henry volatility (defined via partial pressure and liquid-phase mass fraction) of ozone in water at $T = 298.15$ K is $H_V^{pw}(\text{O}_3) = 2.1 \times 10^8$ Pa.

Related term: Henry's law volatility constant

2.2 Conversion between the variants of Henry's law constants

Factors converting variants of Henry's law constants are shown in Tab. 2. An online converter is available at <http://www.henrys-law.org/>.

3 Alternative names and symbols (acceptable, obsolete, and deprecated)

A large number of alternative names for the Henry's law constant can be found in the current scientific literature. For consistency and to avoid confusion, they are listed here.

3.1 Glossary of acceptable, obsolete, and deprecated alternative names for Henry's law constants

3.1.1 absorption coefficient

Note: In the older literature, the term absorption coefficient was sometimes used to describe a constant related to Henry's law. This usage is now considered obsolete, see IUPAC glossary of terms related to solubility [6].

Additional note for Gold Book [7] entry [A00037].

Tab. 2: Factors converting variants of Henry's law constants for a solute B in a binary mixture, assuming ideal gas behavior (R = gas constant, T = temperature, $M(\text{B})$ = molar mass of solute, $M(\text{solv})$ = molar mass of solvent, $\varrho(\text{solv})$ = density of solvent).

A) Conversion between variants of Henry's law solubility constants H_s . For example, $H_s^{cc} = H_s^{cp} \times RT$.				
	$H_s^{cp} =$	$H_s^{xp} =$	$H_s^{bp} =$	$H_s^{cc} =$
$H_s^{cp} \times$	1	$\frac{M(\text{solv})}{\varrho(\text{solv})}$	$\frac{1}{\varrho(\text{solv})}$	RT
$H_s^{xp} \times$	$\frac{\varrho(\text{solv})}{M(\text{solv})}$	1	$\frac{1}{M(\text{solv})}$	$\frac{RT}{M(\text{solv})} \varrho(\text{solv})$
$H_s^{bp} \times$	$\varrho(\text{solv})$	$M(\text{solv})$	1	$RT \varrho(\text{solv})$
$H_s^{cc} \times$	$\frac{1}{RT}$	$\frac{M(\text{solv})}{RT \varrho(\text{solv})}$	$\frac{1}{RT \varrho(\text{solv})}$	1
B) Conversion between variants of Henry's law volatility constants H_v . For example, $H_v^{pc} = H_v^{px} \times RT$.				
	$H_v^{pc} =$	$H_v^{px} =$	$H_v^{pw} =$	$H_v^{cc} =$
$H_v^{pc} \times$	1	$\frac{\varrho(\text{solv})}{M(\text{solv})}$	$\frac{\varrho(\text{solv})}{M(\text{B})}$	$\frac{1}{RT}$
$H_v^{px} \times$	$\frac{M(\text{solv})}{\varrho(\text{solv})}$	1	$\frac{M(\text{solv})}{M(\text{B})}$	$\frac{M(\text{solv})}{RT \varrho(\text{solv})}$
$H_v^{pw} \times$	$\frac{M(\text{B})}{\varrho(\text{solv})}$	$\frac{M(\text{B})}{M(\text{solv})}$	1	$\frac{M(\text{B})}{RT \varrho(\text{solv})}$
$H_v^{cc} \times$	RT	$\frac{RT}{M(\text{solv})} \varrho(\text{solv})$	$\frac{RT}{M(\text{B})} \varrho(\text{solv})$	1
C) Products of Henry's law solubility constants H_s and Henry's law volatility constants H_v . For example, $H_v^{pc} \times H_s^{cc} = RT$.				
	H_s^{cp}	H_s^{xp}	H_s^{bp}	H_s^{cc}
H_v^{pc}	1	$\frac{M(\text{solv})}{\varrho(\text{solv})}$	$\frac{1}{\varrho(\text{solv})}$	RT
H_v^{px}	$\frac{\varrho(\text{solv})}{M(\text{solv})}$	1	$\frac{1}{M(\text{solv})}$	$\frac{RT}{M(\text{solv})} \varrho(\text{solv})$
H_v^{pw}	$\frac{\varrho(\text{solv})}{M(\text{B})}$	$\frac{M(\text{solv})}{M(\text{B})}$	$\frac{1}{M(\text{B})}$	$\frac{RT}{M(\text{B})} \varrho(\text{solv})$
H_v^{cc}	$\frac{1}{RT}$	$\frac{M(\text{solv})}{RT \varrho(\text{solv})}$	$\frac{1}{RT \varrho(\text{solv})}$	1



3.1.2 air-water partition coefficient

Deprecated: The term *dimensionless Henry volatility* and the symbol H_V^{CC} should be used instead.

3.1.3 Bunsen coefficient

Obsolete: In the older literature, the Bunsen coefficient was used to describe a constant related to Henry's law, see IUPAC glossary of terms related to solubility [6].

3.1.4 concentrational solubility coefficient

Deprecated: This term was proposed by the IUPAC clinical chemistry division [2]. It is recommended that the term *Henry's law solubility constant (defined via amount concentration and partial pressure)* and the symbol H_s^{CP} should be used instead.

3.1.5 distribution coefficient

Note: The term distribution coefficient refers to liquid-liquid equilibria [10]. Using it to describe gas-liquid equilibria and Henry's law is deprecated.
Additional note for Gold Book [7] entry [D01812]

3.1.6 distribution constant

Note: The term distribution constant refers to liquid-liquid equilibria [10]. Using it to describe gas-liquid equilibria and Henry's law is deprecated.
Additional note for Gold Book [7] entry [D01813]

3.1.7 distribution ratio

Note: The term distribution ratio refers to liquid-liquid distribution [10]. Using it to describe gas-liquid equilibria and Henry's law is deprecated.
Additional note for Gold Book [7] entry [D01817]

3.1.8 Henry fugacity

Deprecated: The term *Henry volatility* and the symbol H_v should be used instead.

3.1.9 Henry coefficient

Acceptable but the term *Henry's law constant* is preferred.

3.1.10 Henry constant

Acceptable but the term *Henry's law constant* is preferred.

3.1.11 Henry's coefficient

Acceptable but the term *Henry's law constant* is preferred.

3.1.12 Henry's constant

Acceptable but the term *Henry's law constant* is preferred.

3.1.13 Henry's law coefficient

Acceptable but the term *Henry's law constant* is preferred.

3.1.14 Kuenen coefficient

Obsolete: In the older literature, the Kuenen coefficient was used to describe a constant related to Henry's law, see IUPAC glossary of terms related to solubility [6].



3.1.15 molal solubility coefficient

Deprecated: This term was proposed by the IUPAC clinical chemistry division [2]. It is recommended that the term *Henry's law solubility constant (defined via molality and partial pressure)* and the symbol H_s^{bp} should be used instead.

3.1.16 Ostwald coefficient

Deprecated: The Ostwald coefficient was used in the older literature for several, slightly different quantities [11]. Occasionally it is used as a synonym for the *dimensionless Henry's law solubility constant* H_s^{cc} . For details, see IUPAC glossary of terms related to solubility [6].

3.1.17 partition coefficient

Note: The term partition coefficient refers to liquid-liquid distribution [10]. Using it to describe gas-liquid equilibria and Henry's law is deprecated.

Additional note for Gold Book [7] entry [P04437]

3.1.18 partition constant

Note: The term partition constant refers to liquid-liquid distribution [10]. Using it to describe gas-liquid equilibria and Henry's law is deprecated.

Additional note for Gold Book [7] entry [P04438]

3.1.19 rational solubility coefficient

Deprecated: This term was proposed by the IUPAC clinical chemistry division [2] and adopted by the Gold Book [7] [H02783]. It is recommended that the term *Henry's law solubility constant (defined via liquid-phase amount fraction and partial pressure)* and the symbol H_s^{xp} should be used instead.

3.1.20 solubility coefficient

Deprecated: The term solubility coefficient should not be used to refer to Henry's law constants. It could be confused with the very different quantities *solubility* [7] [S05740] and *solubility product* [7] [S05742].

3.1.21 solubility constant

The term solubility constant is a generalization [6] which should not be used to refer to Henry's law constants specifically. It could be confused with the very different quantities *solubility* [7] [S05740] and *solubility product* [7] [S05742].

3.1.22 water-air partition coefficient

Deprecated: The term *dimensionless Henry solubility* and the symbol H_s^{cc} should be used instead.

3.2 Deprecated alternative symbols for Henry's law constants

Given the consistent set of symbols as shown in Fig. 1, the usage of other symbols should be avoided. Thus, several symbols which occur frequently in the current scientific literature are now deprecated:

- The symbol K_H is deprecated, the symbol H should be used instead.
- The symbol k_H (with a lower case letter k) is deprecated as it is internally inconsistent with other IUPAC recommendations. Normally, the lower case letter k describes rate constants, whereas the upper case letter K describes equilibrium constants [8]. Since Henry's law constants are equilibrium constants, the lower case letter k is deprecated.
- The symbol K_{AW} is deprecated; the symbol H_v^{cc} should be used instead.
- The symbol K_{WA} is deprecated; the symbol H_s^{cc} should be used instead.
- The symbol $\alpha_{x,B}^\infty$ is deprecated; the symbol H_s^{xp} should be used instead.
- The acronym "HLC" can be used in a sentence. However, it is not a symbol that can be included in an equation.



4 Related topics

4.1 The solvent

Henry's law has been used mainly for water (or aqueous salt solutions) as solvent. However, there is no need to restrict it to aqueous solutions. The term "Henry's law constant" can also be used for equilibria between the gas phase and a non-aqueous solution. The solvent should always be specified.

The term "Henry's law constant" should not be used to describe equilibria between other phase combinations (e.g., liquid-liquid or gas-solid).

4.2 Temperature dependence

The Henry's law constant is a special case of an equilibrium constant, describing an equilibrium between two phases. To describe the temperature dependence of H_s , the van 't Hoff equation can be used:

$$\frac{1}{H_s} \times \frac{dH_s}{d(1/T)} = \frac{-\Delta_{\text{sol}}H}{R}$$

where $\Delta_{\text{sol}}H$ is the enthalpy of solvation, R is the gas constant and T is the thermodynamic temperature. For a small temperature range, $\Delta_{\text{sol}}H$ can be considered constant. If justified by the accuracy of the measurements, miscellaneous parameterizations can be used to express H_s as a function of T for larger temperature ranges [12].

If the conversion factor between two variants of H includes temperature then these variants have different temperature dependences. For example:

$$\begin{aligned} H_s^{cp} &= H_s^{cc}/(RT) \\ \Rightarrow \frac{1}{H_s^{cp}} \frac{dH_s^{cp}}{d(1/T)} &= \frac{1}{H_s^{cc}} \frac{dH_s^{cc}}{d(1/T)} + T \end{aligned}$$

Consequently, the value of $\Delta_{\text{sol}}H$ also depends on the chosen variant of H :

$$\Delta_{\text{sol}}H(\text{for } H_s^{cp}) = \Delta_{\text{sol}}H(\text{for } H_s^{cc}) - RT$$

An additional but minor effect results from the temperature dependence of the density of the solution. This affects Henry's law constants based on concentration c but not those based on molality b , amount fraction x or mass fraction w .

Whenever relating a thermodynamic quantity to a Henry's law constant, it is necessary to specify which variant of Henry's law constant it refers to and which standard states it is based upon.

4.3 Activity coefficients and experimental Henry's law constants

When defining Henry's law constants for a two-component (solvent + solute) system, there is no need to consider any non-ideality because Henry's law constants refer to infinite dilution where activity and fugacity coefficients approach unity. Non-ideal behaviour can be accounted for by using activity coefficients for the solution and fugacity coefficients for the gas phase [13].

Infinite dilution is of course a hypothetical state, and measurements can be performed only at non-zero abundances. An "experimental Henry's law constant" can be defined as, e.g.:

$$H_{s,\text{exp}}^{cp} = \frac{c_1}{p}$$

where c_1 and p are the measured liquid-phase concentration and partial pressure of the solute, respectively. Due to non-ideality, the experimental Henry's law constant is not a true constant but depends on the solute concentration. From measurements at different abundances, the Henry's law constant can be determined by extrapolation to infinite dilution. For example, for H_s^{cp} :

$$H_s^{cp} = \lim_{c_1 \rightarrow 0} H_{s,\text{exp}}^{cp} = \lim_{c_1 \rightarrow 0} \frac{c_1}{p}$$

4.4 Effective Henry's law constant

If a Henry's law constant refers to exactly the same species in the gas phase and in the solution, it is called the "intrinsic" Henry's law constant (sometimes, the terms "physical" or "species" Henry's law constant are used). If a Henry's law constant refers to the sum of several species in solution which result via fast equilibrium, it is called the "effective" Henry's law constant (sometimes, the terms "apparent" or "stoichiometric" Henry's law constant are used). An effective Henry's law constant should not be used when the equilibration of the dissolved species is slow relative to other processes being considered, for example, diffusion or chemical reaction in solution. When referring to an effective Henry's law constant, "eff" should be added to the subscript of the symbol.

Taking methanal (formaldehyde, HCHO) as an example, the intrinsic Henry's law constant can be written as:

$$H_s^{cp} = \lim_{c \rightarrow 0} \frac{c(\text{HCHO})}{p(\text{HCHO})}$$

In aqueous solutions, HCHO is in equilibrium with its hydrated form:



Here, HCHO denotes the unhydrated, physically dissolved species. The total of the unhydrated and the hydrated form is:



Thus, the effective Henry's law constant of HCHO is:

$$H_{\text{s,eff}}^{\text{cp}} = \lim_{c \rightarrow 0} \frac{c(\text{HCHO}_{\text{tot}})}{p(\text{HCHO})} = \lim_{c \rightarrow 0} \frac{c(\text{HCHO}) + c(\text{H}_2\text{C}(\text{OH})_2)}{p(\text{HCHO})}$$

The relation between the intrinsic and the effective Henry's law constant for HCHO is:

$$H_{\text{s,eff}}^{\text{cp}} = H_{\text{s}}^{\text{cp}} \times (1 + K_{\text{hyd}})$$

where $K_{\text{hyd}} = \lim_{c \rightarrow 0} c(\text{H}_2\text{C}(\text{OH})_2)/c(\text{HCHO})$ is the hydration equilibrium constant at infinite dilution. Both the intrinsic and the effective Henry's law constant describe a linear proportionality between the phases.

Effective Henry's law constants are also used for chemicals that undergo ionic dissociation upon dissolution. For acids and bases, it can be desired to determine the total of the dissolved species (undissociated dissolved gas plus ionic dissociation species). For example, the effective Henry's law constant of hypochlorous acid (HOCl) is:

$$H_{\text{s,eff}}^{\text{cp}} = \lim_{c \rightarrow 0} \frac{c(\text{HOCl}) + c(\text{ClO}^-)}{p(\text{HOCl})}$$

Considering the acidity constant at infinite dilution

$$K_{\text{a}} = \lim_{c \rightarrow 0} c(\text{H}^+) \times c(\text{ClO}^-)/c(\text{HOCl})$$

the relation between the intrinsic and the effective Henry's law constant for HOCl can be calculated as:

$$H_{\text{s,eff}}^{\text{cp}} = H_{\text{s}}^{\text{cp}} \times \left(1 + \frac{K_{\text{a}}}{c(\text{H}^+)} \right)$$

Since the factor on the right hand side contains $c(\text{H}^+)$, the conversion between the intrinsic and the effective Henry's law constant is pH-dependent. Proportionality between $p(\text{HOCl})$ and the total dissolved hypochlorous acid ($c(\text{HOCl}) + c(\text{ClO}^-)$) is restricted to conditions under which the uptake of gaseous HOCl does not affect the acidity of the solution. Effective Henry's law constants of acids and bases are not material constants but depend on the solution pH.

4.5 Product of the Henry's law constant and the acidity constant

Sometimes, especially for strong acids, the product of the Henry's law constant (H_s^{cp}) and the acidity constant at infinite dilution (K_a) is presented, e.g.:

$$H_s^{cp} \times K_a = \lim_{c \rightarrow 0} \frac{c(\text{HCl})}{p(\text{HCl})} \times \frac{c(\text{H}^+) \times c(\text{Cl}^-)}{c(\text{HCl})} = \lim_{c \rightarrow 0} \frac{c(\text{H}^+) \times c(\text{Cl}^-)}{p(\text{HCl})}$$

With the (difficult to measure) concentration of undissociated HCl canceling out, the overall equilibrium constant $H_s^{cp} K_a$ can be determined more accurately than the individual factors H_s^{cp} and K_a [14]. In addition, it is this overall equilibrium constant that is normally the quantity of interest.

The product $H_s^{cp} K_a$ is sometimes also called a “Henry's law constant”. However, as there is no proportionality between $c(\text{Cl}^-)$ and $p(\text{HCl})$, the product should not be called a “Henry's law constant” [15].

4.6 Infinite dilution activity coefficient

Dividing the Henry's law volatility constant H_v^{px} by the saturation vapour pressure p^* of the solute yields the infinite dilution activity coefficient γ^∞ (also called limiting activity coefficient):

$$\gamma^\infty = \frac{H_v^{px}}{p^*}$$

It can only be defined below the critical temperature of the solute. Note that γ^∞ is referenced to Raoult's law, not Henry's law².

2 In representing the thermodynamics of solutions, two conventions, one symmetric and the other unsymmetric, are used. In the symmetric convention all components are treated similarly, the reference states for the components are the pure substances at the relevant temperature and pressure and, in an ideal solution, all components obey Raoult's law ($p = xp^*$, where x is the amount fraction of the solute in the solution, p its partial pressure in the gas phase, and p^* is the saturated vapor pressure of the pure component). In the unsymmetric or dilute solution convention, the solvent is treated in the same way but the reference states for the solutes are hypothetical solutions having unit concentration but the energetic properties of an infinitely dilute solution. In the ideal dilute solution the solvent obeys Raoult's law but the solutes obey Henry's law. In both conventions non-ideality is accounted for by the inclusion of activity coefficients, which reflect deviations from the relevant ideality. Thus, for some solute amount fraction x one can write: $p = x\gamma_x H_v^{px} = xf p^*$ where the activity coefficients γ_x and f are referenced to Henry's law and Raoult's law, respectively. So $f = \gamma_x H_v^{px} / p^*$ and in the case of the infinitely dilute solution, where $\gamma_x = 1$ and $f = \gamma^\infty$, we obtain $\gamma^\infty = H_v^{px} / p^*$ giving $f = \gamma_x \gamma^\infty$ for any solute concentration, x .



4.7 Value at a reference temperature

Like other thermodynamic quantities, Henry's law constants are often measured and presented at a temperature of $T = 298.15$ K. IUPAC has recommended this value as the reference temperature for thermodynamic data [16]. However, since other temperatures (e.g., 273.15 K or 293.15 K) are also occasionally used, it is always necessary to state the chosen value [13]. To indicate the temperature, it can be added to the symbol in parentheses, e.g.: $H_s(298.15 \text{ K})$.

4.8 Sechenov equation

Values of Henry's law constants depend on the composition of the solution, e.g., on the ionic strength of a salt solution. In general, the solubility of a gas decreases with increasing salinity ("salting out"). This effect is described by the Sechenov equation [17]. There are many ways to define the Sechenov equation, depending on how the composition of the liquid phase is described (based on concentration, molality, or amount fraction) and which variant of the Henry's law constant is used. One possibility is:

$$\log_{10} \left(\frac{H_{s0}^{bp}}{H_s^{bp}} \right) = K_s \times b(\text{salt})$$

where H_{s0}^{bp} = Henry's law constant for pure water, H_s^{bp} = Henry's law constant for the salt solution, K_s = molality-based Sechenov parameter, and $b(\text{salt})$ = molality of the salt solution.

4.9 Obtaining Henry's law constants

Critical reviews of many Henry's law constants have been published in the IUPAC Solubility Data Series [5]. Another source is the compilation of Henry's law constants [12], which is also available on the internet as a searchable database (<http://www.henrys-law.org/>).

4.10 Glossary of related topics

4.10.1 effective Henry's law constant, H_{eff}

Synonyms: apparent Henry's law constant, stoichiometric Henry's law constant
If a Henry's law constant refers to the sum of several species in solution which

result via fast equilibrium, it is called *effective Henry's law constant*.

Example 1: The effective Henry's law constant of HCHO not only considers dissolved HCHO but also the hydrated form $\text{H}_2\text{C}(\text{OH})_2$.

Example 2: The effective Henry's law constant of HOCl not only considers dissolved HOCl but also its conjugate base ClO^- .

Related term: intrinsic Henry's law constant

4.10.2 intrinsic Henry's law constant

Synonyms: physical Henry's law constant, species Henry's law constant

To emphasize that a Henry's law constant refers to exactly the same species in the gas phase and in solution, and to distinguish it from the *effective Henry's law constant*, it can be called *intrinsic Henry's law constant*.

Related term: effective Henry's law constant

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