Henry's law constant and related coefficients for aqueous hydrocarbons, CO_2 and H_2S over a wide range of temperature and pressure

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ABSTRACT

This article presents three interrelated topics. First, the Henry's law constant (HLC) and its use are reviewed in a broader thermodynamic context reaching beyond the restricted image of HLC as a coefficient reflecting partitioning between liquid and vapor phases. The relationships of HLC to the vapor–liquid distribution coefficient and the air–water partition coefficient are discussed as well as the interrelation between expressions of HLC in terms of different concentration scales. Second, the previously published group contribution method for estimation of HLC of hydrocarbons [J. Sedlbauer, G. Bergin, V. Majer, AIChE J. 48 (2002) 2936] is extended by adding the newly determined parameters for CH_4, CO_2 and H_2S. Inclusion of these three major constituents of the natural gas makes the method more versatile in application to systems where oil and/or natural gas coexist with an aqueous phase. When establishing the parameters of the model the representative HLCs from literature were combined with the data on the derivative properties available over a wide range of conditions from the calorimetric and volumetric experiments. An attention is paid particularly to the effect of pressure on the HLC. Third, a convenient user-friendly software package is described allowing calculation of HLC and of other related coefficients over a wide range of temperature and pressure on the basis of the presented model. This package is available on request in an executable form on a shareware basis for non-commercial users.

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1. Introduction

The Henry's law constant K_H is a quantity frequently applied in the thermodynamic description of dilute aqueous solutions. It was originally proposed more than 200 years ago [1] as a measure of gas solubility in a liquid, and expressed as a ratio of the partial pressure of a gaseous solute to its equilibrium concentration in the liquid phase. The perception and use of the Henry's law constant today is, however, much broader; from the physicochemical point of view K_H is basically a coefficient relating the fugacity of a dissolved nonelectrolyte to its concentration in a solution. The solute can be in the pure state gaseous, liquid or solid and solvent is often water. The Henry's law constant is namely used in environmental chemistry and atmospheric physics as a major criterion for describing air–water partitioning of solutes at near-ambient conditions. It plays a major role in evaluating the transport of pollutants between atmosphere and aquatic systems, rain water

and aerosols. The Henry's law constant is also used extensively in chemical engineering and geochemistry for designing or describing processes where dilute aqueous systems are involved, often over a wide range of temperature and pressure. In this case it is necessary to adopt some theoretically founded concepts allowing a realistic calculation of the Henry's law constant at superambient conditions.

The use of the Henry's law constant by different communities is reflected by the establishment of multiple and alternative definitions of this quantity, leading to a considerable confusion in literature. Thus, the Henry's law constant is certainly a coefficient the most frequently applied in phase equilibrium calculations concerning dilute solutions, but its thermodynamic essence is often misunderstood or misinterpreted. For that reason we have found useful to present in the first part of this paper a concise review of the thermodynamics regarding the Henry's law constant and to show how the different versions of K_H and other related coefficients are interconnected.

An effort has been made over the past years to use the QSPR[1] concepts for building up linear prediction schemes for the Henry's

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[1] QSPR quantitative structure–property relationship.

law constant, covering a variety of organic solutes in water. After the pioneering work of Hine and Mookerjee [2] this approach has become namely popular in environmental chemistry where different methods using fragmentary contributions [3], topological descriptors [4,5] or solvochromic parameters [6–8] have been used for estimations at 298 K. In addition, more sophisticated, yet mainly empirical, computational models were introduced recently using quantum mechanical descriptors [9–11] and advanced statistical techniques based on neural networks [12–14]. While all these schemes are designed for predictions at near-ambient conditions, the methods for estimation of the Henry's law constant as a function of temperature are limited. Sedlbauer et al. [15] have published a model allowing calculation of the Henry's law constant for aqueous C_2 to C_{12} hydrocarbons over a wide range of temperature ($273 < T < 573$ K) and pressure ($0.1 < p < 100$ MPa). The group contribution approach was used for calculating the parameters of a thermodynamically sound model for infinite dilution properties [16] allowing to obtain K_H via the Gibbs energy of hydration.

Besides clarifying various concepts of the Henry's law constant this article has basically two objectives. First, the previously published estimation method of Sedlbauer and collaborators is extended by adding the parameters for CH_4, CO_2 and H_2S. Inclusion of these three major constituents of the natural gas encountered frequently in the presence of other hydrocarbons ($N_C > 2$) makes the method more versatile for phase equilibrium calculations in systems where oil and/or natural gas coexist with an aqueous phase. When establishing the parameters for these three gaseous solutes we have combined the representative Henry's law constants selected recently by Fernandez-Prini et al. [17] with the data on the derivative properties available over a wide range of conditions from the calorimetric and volumetric experiments. An attention is paid particularly to the effect of pressure on the Henry's law constant of gases and liquids.

Second, a convenient user-friendly software package is described allowing calculation of the Henry's law constant and several related coefficients characterizing vapor–liquid equilibria over a wide range of conditions. This package is available on request in an executable form on a shareware basis for noncommercial users. Availability of such a software tool is important for implementation of the method. The reprogramming of the model would be complex, requiring, e.g. the use of the same fundamental EOS for water as that applied when establishing the group contributions for calculating the parameters of the model.

2. Thermodynamic background

The aim of the following outline of basic equations is to present the Henry's law constant in a broader thermodynamic context going beyond its restrictive viewing as a coefficient reflecting partitioning between the liquid and vapor phases, as well as to elucidate the interrelation between the related coefficients defined in terms of different concentration scales.

The Henry's law constant K_H is defined in modern chemical thermodynamics as the limiting fugacity/molar fraction ratio of a solute in a solution [18,19] and has therefore the dimension of pressure

$$K_H[T, p] = \lim_{x_s \to 0} \left(\frac{f_s}{x_s} \right) \tag{1}$$

Fugacity of the solute f_s and its molar fraction x_s relate to the same phase, thus this is a one-phase definition of the Henry's law constant without assumption of any kind of the phase equilibrium

condition. For that reason it is a function of two independent variables, temperature and pressure.[2]

The chemical potential of a solute in a solution (the partial molar Gibbs energy, $\bar{G}_s$) can be expressed depending on the choice of the standard state ($G_s^{ig}[T, p_{ref}]$ for ideal gas at a reference pressure $p_{ref} = 0.1$ MPa, or $G_s^{\circ}[T, p]$ for infinitely dilute solution[3]) as

$$\bar{G}_s[T, p] = G_s^{ig}[T, p_{ref}] + RT \ln \left(\frac{f_s}{p_{ref}} \right) = G_s^{\circ}[T, p] + RT \ln(x_s \gamma_s^H) \tag{2}$$

The symbol γ_s^H stands for the dimensionless activity coefficient compatible with the Henry's law, i.e. $\lim_{x_s \to 0} \gamma_s^H = 1$ Combination of Eqs. (1) and (2) in the limit of infinite dilution leads to the expression

$$RT \ln \left(\frac{K_H[T, p]}{p_{ref}} \right) = G_s^{\circ}[T, p] - G_s^{ig}[T, p_{ref}] = \Delta G_{hyd}^{\circ}[T, p] \tag{3}$$

where ΔG_{hyd}° is the Gibbs energy of hydration corresponding to the transfer of a solute from an ideal gas state to an infinitely dilute solution.

For description of solutions, other concentration variables are sometimes preferred to the molar fraction x_s. These are namely molality m_s (mol/kg) popular with geochemists or molarity c_s (mol/m^3) used often in environmental science. It holds in the limit of infinite dilution

$$\lim_{x_s \to 0} m_s = \frac{x_s}{M_w} \quad \text{and} \quad \lim_{x_s \to 0} c_s = \frac{x_s \rho_w}{M_w} \tag{4}$$

where M_w (kg/mol) and ρ_w (kg/m^3) are the molar mass and density of water, respectively. The values of the standard state chemical potentials are therefore affected by the choice of the concentration variable as follows

$$G_{sm}^{\circ} = G_{sx}^{\circ} + RT \ln(M_w m_o) \quad \text{and} \quad G_{sc}^{\circ} = G_{sx}^{\circ} + RT \ln \left(\frac{M_w c_o}{\rho_w} \right) \tag{5}$$

Since activity coefficients are always dimensionless, the standard concentrations $m_o = 1$ mol/kg and $c_o = 1$ mol/m^3 must be introduced for converting molality and molarity to dimensionless concentration variables. Introduction of Eq. (5) into Eq. (3) then leads to the relationship between K_H and the alternative definitions of the Henry's law constant in terms of molality K_{Hm} and molarity K_{Hc}. It holds:

$$K_{Hm} = \lim_{m_s \to 0} \left(\frac{f_s}{m_s/m_o} \right) = K_{Hx} M_w m_o \quad \text{and}$$

$$K_{Hc} = \lim_{c_s \to 0} \left(\frac{f_s}{c_s/c_o} \right) = K_{Hx} M_w \frac{c_o}{\rho_w} \tag{6}$$

This means that both K_{Hm} and K_{Hc} have also dimension of pressure and are thus consistent with Eqs. (3) and (5). In practical use, the alternative Henry's law constants are, however, usually expressed simply as a ratio of pressure to molality or molarity. While this is not strictly rigorous in the light of the above relationships, this simplified convention allows to distinguish immediately what concentration scale was selected and is therefore generally used in applications.

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[2] The definition of the Henry's law constant introduced here is of course more general than that resulting from the "historical understanding" of K_H exclusively as a parameter reflecting the gas solubility. When the Henry's law constant is obtained experimentally from the vapor–liquid equilibrium measurements it is related logically to the vapor pressure of the solvent due to the limit of infinite dilution.

[3] This standard state adopted for aqueous species is unit activity in a hypothetical solution of unit concentration referenced to infinite dilution (denoted with superscript '$\circ$').