



# Henry's law constant and related coefficients for aqueous hydrocarbons, CO<sub>2</sub> and H<sub>2</sub>S 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<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S. 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 physico-chemical 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<sup>1</sup> concepts for building up linear prediction schemes for the Henry's

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<sup>1</sup> 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 solvchromic 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<sub>2</sub> to C<sub>12</sub> 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<sub>H</sub> 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<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S. Inclusion of these three major constituents of the natural gas encountered frequently in the presence of other hydrocarbons (N<sub>C</sub> > 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 non-commercial 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<sub>H</sub> 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

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

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.<sup>2</sup>

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 ( $G_s^{\text{ig}}[T, p_{\text{ref}}]$  for ideal gas at a reference pressure  $p_{\text{ref}} = 0.1$  MPa, or  $G_s^{\circ}[T, p]$  for infinitely dilute solution<sup>3</sup>) as

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

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

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

where  $\Delta G_{\text{hyd}}^{\circ}$  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<sup>3</sup>) used often in environmental science. It holds in the limit of infinite dilution

$$\lim_{x_s \rightarrow 0} m_s = \frac{x_s}{M_w} \quad \text{and} \quad \lim_{x_s \rightarrow 0} c_s = \frac{x_s \rho_w}{M_w} \quad (4)$$

where  $M_w$  (kg/mol) and  $\rho_w$  (kg/m<sup>3</sup>) 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

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

Since activity coefficients are always dimensionless, the standard concentrations  $m_o = 1$  mol/kg and  $c_o = 1$  mol/m<sup>3</sup> 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<sub>H</sub> and the alternative definitions of the Henry's law constant in terms of molality K<sub>Hm</sub> and molarity K<sub>Hc</sub>. It holds:

$$K_{Hm} = \lim_{m_s \rightarrow 0} \left( \frac{f_s}{m_s/m_o} \right) = K_{Hx} M_w m_o \quad \text{and} \quad K_{Hc} = \lim_{c_s \rightarrow 0} \left( \frac{f_s}{c_s/c_o} \right) = K_{Hx} M_w \frac{c_o}{\rho_w} \quad (6)$$

This means that both K<sub>Hm</sub> and K<sub>Hc</sub> 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.

<sup>2</sup> The definition of the Henry's law constant introduced here is of course more general than that resulting from the "historical understanding" of K<sub>H</sub> 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.

<sup>3</sup> This standard state adopted for aqueous species is unit activity in a hypothetical solution of unit concentration referenced to infinite dilution (denoted with superscript "o").

The derivatives of Eq. (3) allow establishing the exact thermodynamic relationships describing the temperature and pressure dependence of the Henry's law constant. It holds:

$$RT^2 \left( \frac{\partial \ln K_H}{\partial T} \right)_p = -(H_s^\circ[T, p] - H_s^{\text{ig}}[T, p_{\text{ref}}]) = -\Delta H_{\text{hyd}}^\circ \quad (7)$$

$$\left( \frac{\partial}{\partial T} \left[ RT^2 \frac{\partial \ln K_H}{\partial T} \right] \right)_p = -(C_{p,s}^\circ[T, p] - C_{p,s}^{\text{ig}}[T, p_{\text{ref}}]) = -\Delta C_{p,\text{hyd}}^\circ \quad (8)$$

$$RT \left( \frac{\partial \ln K_H}{\partial p} \right)_T = V_s^\circ[T, p]. \quad (9)$$

The standard thermodynamic properties (enthalpy, heat capacity and volume) of solute relate to an ideal gas ( $H_s^{\text{ig}}, C_{p,s}^{\text{ig}}$ ) or an infinitely dilute solution ( $H_s^\circ, C_{p,s}^\circ, V_s^\circ$ ). It follows from Eqs. (7) and (8) that the temperature dependence of the Henry's law constant can be calculated by integrating the derivative hydration properties ( $\Delta H_{\text{hyd}}^\circ, \Delta C_{p,\text{hyd}}^\circ$ ) that are accessible from calorimetric and spectroscopic measurements. Enthalpy of hydration  $\Delta H_{\text{hyd}}^\circ$  is calculated as a combination of heat of solution and the residual enthalpy (difference between the enthalpy of pure solute and that of an ideal gas) that is in absolute value close to the enthalpy of vaporization for liquid solutes. The heat capacity of hydration  $\Delta C_{p,\text{hyd}}^\circ$ , calculated as a difference of solute heat capacity at infinite dilution and that of an ideal gas, is positive and increasing with temperature for volatile nonelectrolytes [20].  $\Delta H_{\text{hyd}}^\circ$  values, generally negative at near-ambient conditions, become positive at high temperatures, scaling with water expansivity and diverging when approaching the critical point of water. The Henry's law constant is therefore at first increasing with temperature, exhibiting a maximum typically between 373 and 473 K, and decreasing with temperature when approaching the critical point of water.

Similarly the change of the Henry's law constant with pressure can be calculated by integrating Eq. (9) where the partial molar volume at infinite dilution of a solute  $V_s^\circ$  is accessible from densitometric measurements. Its value is proportional to the molar mass of solute at room temperature and scales with compressibility of water at conditions remote from ambient, diverging positively at the critical point of water for volatile nonelectrolytes [20]. The Henry's law constant is therefore generally increasing with increasing pressure. The integral of Eq. (9) between saturation pressure of the solvent and pressure of the system is identical with the Krichevski–Kasarnovsky equation used in the chemical engineering literature for calculating the so-called Poynting correction expressing the change of fugacity with pressure.

It is apparent from the combination of Eqs. (6)–(9) that  $K_{Hm}$  and  $K_H$  have identical temperature and pressure slopes while a minor difference is observed in the case of  $K_{Hc}$  where the mechanical coefficients of water (expansivity and compressibility) play a role.

The Henry's law constant is used mainly for the description of vapor (or gas)–liquid equilibria and the compositions of coexisting phases ( $y_s$  and  $x_s$ ) obtained from experiments are at the same time also the major data source for determining  $K_H$  of volatile solutes:

$$py_s \varphi_s = K_H[T, p_w^{\text{sat}}] \exp \left( \int_{p_w^{\text{sat}}}^p \frac{V_s^\circ[T, p]}{RT} dp \right) x_s \gamma_s^{\text{H}}. \quad (10)$$

The symbols  $p$ ,  $\varphi_s$  and  $p_w^{\text{sat}}$  denote the overall pressure, the fugacity coefficient of a solute in the vapor and the saturation pressure of water, respectively. Since the Henry's law constant is defined in the limit of infinite dilution (Eq. (1)), it can be obtained from experimental vapor–liquid equilibrium data when  $p \rightarrow p_s^{\text{sat}}$ . Then in the above relationship both the exponential term (the Poynting correction) and  $\gamma_s^{\text{H}}$  approach unity. The temperature dependence of the

Henry's law constant is therefore mostly presented in the literature along the saturation line of water and for that reason some authors maintain that  $K_H$  is a function of one independent variable only—temperature (e.g. [21–23]). This statement is, however, not quite correct considering the direct link of the Henry's law constant with the Gibbs energy of hydration and implying a general validity of Eq. (9). It is in principle always possible to construct the thermodynamic surface of  $K_H[T, p]$  with two independent state variables. The limited amount of the volumetric data for aqueous solutes, especially at superambient conditions, is, however, a major obstacle. Without this information it is difficult to separate in Eq. (10) the effect of pressure on the Henry's law constant from the nonideality of aqueous solution since the concentration of solute  $x_s$  is increasing due to increasing pressure and the solution cannot then be considered as ideal ( $\gamma_s^{\text{H}} \neq 1$ ). This interconnection between the Poynting and nonideality corrections hampers the use of high-pressure vapor–liquid equilibrium data for  $K_H$  determination [65].

The Henry's law constant of sparingly soluble liquids or solids in water is determined from their solubilities  $x_s^{\text{sol}}$  in water as follows:

$$p_s^{\text{sat}} \varphi_s^{\text{sat}} \exp \left( \frac{V_s^\circ (p - p_s^{\text{sat}})}{RT} \right) \cong K_H[T, p] x_s^{\text{sol}} \quad (11)$$

where  $p_s^{\text{sat}}$  and  $V_s^\circ$  are the vapor pressure and molar volume of pure solute, respectively. This equation is valid for low solubilities where  $\gamma_s^{\text{H}} \approx 1$  and in the cases where the solubility of water in the nonaqueous phase can be neglected. Since the volume of a condensed solute changes little with pressure, this equation is a good approximation that allows to calculate the Henry's law constant as a function of both temperature and pressure. At low pressures it simply holds that  $K_H \cong p_s^{\text{sat}}/x_s^{\text{sol}}$ , this relationship being the main avenue used for calculating the Henry's law constant of low volatility solutes that are sparingly soluble in water.

The symmetrical limiting activity coefficients  $\gamma_s^{\text{R}\infty}$  complying with the Raoult's law ( $\lim_{x_s \rightarrow 1} \gamma_s^{\text{R}} = 1$ ) are extensively used in engineering thermodynamics for describing nonideality of dilute solutions at temperatures up to 373 K and at ambient pressure. Their determination from the phase equilibrium data is carried out typically *via* the Henry's law constant or related coefficients defined below. Since the fugacity of a solute in the liquid phase can be expressed as  $f_s = f_s^* x_s \gamma_s^{\text{R}}$ , the combination with Eq. (1) gives

$$K_H = f_s^* \gamma_s^{\text{R}\infty} = p_s^{\text{sat},l} \gamma_s^{\text{R}\infty} \quad (12)$$

where  $f_s^*$  and  $p_s^{\text{sat},l}$  are the fugacity and saturation vapor pressure of a real or hypothetical liquid solute.

Several other coefficients closely related to  $K_H$  were introduced for describing the partitioning of solutes between the vapor and liquid phases. This is the case of the vapor–liquid distribution coefficient  $K_d$  (denoted sometimes also as the limiting relative volatility  $\alpha$ ) that is defined as

$$K_d = \lim_{x_s \rightarrow 0} \left( \frac{y_s}{x_s} \right) \quad (13)$$

It follows immediately from Eq. (10) for a binary system consisting of a solute and water

$$K_d = \frac{K_H[T, p_w^{\text{sat}}]}{p_w^{\text{sat}} \varphi_w^{\text{sat}}} \quad (14)$$

where  $\varphi_w^{\text{sat}}$  is the fugacity coefficient of saturated water vapor. It means that  $K_d$  corresponds simply to the ratio of the Henry's law constant and saturation vapor pressure at conditions where vapor phase nonideality can be neglected. Coefficient  $K_d$  is logically defined exclusively along the saturation line of solvent.

The Henry's law constant is often considered in geochemistry and atmospheric physics as a thermodynamic reaction constant

corresponding to a hydration process where the solute is transferred from an ideal gas state to an ideal aqueous solution with the standard states defined in terms of unit molality or molarity. Thus, the following two coefficients

$$K'_{Hm} = \frac{m_s}{p_s} \cong \frac{m_o}{K_{Hm}} \quad \text{and} \quad K'_{Hc} = \frac{c_s}{p_s} \cong \frac{c_o}{K_{Hc}} \quad (15)$$

are encountered in literature. The symbol  $p_s$  is the partial pressure of a solute in the vapor phase and the concentration variables express concentration of the solute in the aqueous phase.

The air–water partition coefficient  $K_{aw}$  characterizing equilibrium distribution of a solute between the atmospheric and aqueous phases is defined as the limiting molarity ratio

$$K_{aw} = \lim_{c_s^w \rightarrow 0} \left( \frac{c_s^a}{c_s^w} \right), \quad (16)$$

where  $c_s^a$  and  $c_s^w$  are the equilibrium concentrations of a solute in air and water, respectively. This coefficient is sometimes called in environmental chemistry the dimensionless Henry's law constant. In the limit of infinite dilution it holds for the aqueous phase  $c_s^w = x_s^w \rho_w / M_w$  and the atmospheric phase can be approximated by an ideal gas equation of state,  $c_s^a = p_s^a / RT$  where  $p_s^a$  is the partial pressure of solute in the air. Since at atmospheric conditions  $p_s^a = K_H x_s^w$ , it holds

$$K_{aw} = \frac{K_H M_w}{RT \rho_w} = \frac{K_{Hm}}{RT \rho_w m_o} = \frac{K_{Hc}}{RT c_o} \quad (17)$$

This coefficient  $K_{aw}$  is presented typically at 298 K or over a limited temperature interval at near-ambient conditions. Taking into account Eq. (7) it follows for the temperature dependence of  $K_{aw}$ :

$$\left( \frac{\partial \ln K_{aw}}{\partial T} \right)_p = \left( \frac{\partial \ln K_H}{\partial T} \right)_p + \kappa_w - \frac{1}{T} = \frac{-\Delta H_{hyd}^\circ / RT + T \kappa_w - 1}{T} \quad (18)$$

where  $\kappa_w$  is water compressibility. At temperatures close to ambient  $-\Delta H_{hyd}^\circ / RT$  and  $T \kappa_w$  are of the order of 10 and 0.1, respectively. Then the above relationship suggests that the temperature slope of  $K_{aw}$  is about 10% lower compared to that for  $K_H$ .

### 3. Description of the group contribution method for $K_H$

The Henry's law constants is calculated as a function of temperature and pressure via the Gibbs energy of hydration that can be expressed as follows [24]

$$RT \ln \left( \frac{K_H}{p_{ref}} \right) = \Delta G_{hyd}^\circ [T, p] = \Delta G_{hyd}^\circ [T_{ref}, p_{ref}] - (T - T_{ref}) \Delta S_{hyd}^\circ [T_{ref}, p_{ref}] + \int_{T_{ref}}^T (\Delta C_{p,hyd}^\circ)^{p_{ref}} dT - T \int_{T_{ref}}^T (\Delta C_{p,hyd}^\circ)^{p_{ref}} d \ln T + \int_{p_{ref}}^p (V_s^\circ)^T dp \quad (19)$$

where  $\Delta G_{hyd}^\circ [T_{ref}, p_{ref}]$  and  $\Delta S_{hyd}^\circ [T_{ref}, p_{ref}]$  are the terms relating to the reference state at  $T_{ref} = 298.15$  and  $p_{ref} = p^\circ = 0.1$  MPa. The entropic term is typically obtained as

$$\Delta S_{hyd}^\circ [T_{ref}, p_{ref}] = \frac{\Delta H_{hyd}^\circ [T_{ref}, p_{ref}] - \Delta G_{hyd}^\circ [T_{ref}, p_{ref}]}{T_{ref}} \quad (20)$$

using the Gibbs energy and enthalpy reference state data. The three integrals express the change with temperature and pressure, the superscripts  $p_{ref}$  and  $T$  indicate the constant variable at which the integration is performed. We have adopted an approach combining two distinct schemes; one for calculating the values of

**Table 1**

Group contributions for calculating  $\Delta G_{hyd}^\circ [T_{ref}, p_{ref}]$  and  $\Delta S_{hyd}^\circ [T_{ref}, p_{ref}]$ ; values of group contributions for hydrocarbons  $C_2$  and higher are from lit [25]; values for  $CH_4$ ,  $CO_2$  and  $H_2S$  are obtained from the data in lit [17,26]

Functional group	$\Delta G_{hyd}^\circ [T_{ref}, p_{ref}]$ (kJ mol <sup>-1</sup> )	$\Delta S_{hyd}^\circ [T_{ref}, p_{ref}]$ (J mol <sup>-1</sup> K <sup>-1</sup> )
$Y_{SS}^a$	17.92	-67.78
C	-4.50	23.81 <sup>b</sup>
CH	-1.79	2.99 <sup>b</sup>
CH <sub>2</sub>	0.72	-15.03 <sup>b</sup>
CH <sub>3</sub>	3.63	-37.46 <sup>b</sup>
C=C	-10.23	36.32 <sup>b</sup>
H <sub>T</sub> <sup>c</sup>	3.91	-25.52 <sup>b</sup>
c-CH <sup>d</sup>	-1.03	-4.60 <sup>b</sup>
c-CH <sub>2</sub>	0.83	-20.76 <sup>b</sup>
C <sub>ar</sub> <sup>e</sup>	-3.85	10.67 <sup>b</sup>
CH <sub>ar</sub>	-0.65	-14.59 <sup>b</sup>
I(C-C) <sup>f</sup>	-1.01	10.10 <sup>b</sup>
CH <sub>4</sub>	8.283	-64.04 <sup>b</sup>
CO <sub>2</sub>	0.421	-59.80 <sup>b</sup>
H <sub>2</sub> S	-2.358	-44.78 <sup>b</sup>

<sup>a</sup> The standard state term to be used as  $\Delta Y_{hyd}^\circ [T_{ref}, p_{ref}] = Y_{SS} + \sum_{i=1}^N n_i Y_{s,i}^\circ$  where  $\Delta Y_{s,i}^\circ$  are individual group contributions and  $n_i$  is the number of their occurrences in the molecule. Standard state term is also used in the case of  $CH_4$ ,  $CO_2$  and  $H_2S$ .

<sup>b</sup> Entropic group contributions were calculated from Eq. (20).

<sup>c</sup> Hydrogen atom bound to alkene group.

<sup>d</sup> Prefix c denotes a cycloalkane group.

<sup>e</sup> Group with subscript ar is a part of aromatic ring.

<sup>f</sup> Correction for *ortho* position on aromatic ring.

$\Delta G_{hyd}^\circ [T_{ref}, p_{ref}]$  and  $\Delta S_{hyd}^\circ [T_{ref}, p_{ref}]$ , and the second for expressing the three integrals in Eq. (19).

The Gibbs energy and entropy of hydration at the reference state  $T_{ref}, p_{ref}$  are obtained for hydrocarbons ( $C_2$  and higher) from the group contributions for  $\Delta G_{hyd}^\circ [T_{ref}, p_{ref}]$  and  $\Delta S_{hyd}^\circ [T_{ref}, p_{ref}]$  tabulated by Plyasunov and Shock [25]. In the case of  $CH_4$ ,  $CO_2$  and  $H_2S$   $\Delta G_{hyd}^\circ [T_{ref}, p_{ref}]$  was calculated from the Henry's law constant at 298.15 K obtained from the evaluated data by Fernandez-Prini et al. [17] using Eq. (3). The  $\Delta S_{hyd}^\circ [T_{ref}, p_{ref}]$  values are those recommended by Plyasunov et al. [26]. Table 1 lists the concrete Gibbs energy and entropy of hydration values: the first line contains the intrinsic  $Y_{SS}$  values that correspond to the material point contribution to the Gibbs energy and entropy of hydration. This term is derived from statistical mechanics [27] and can be calculated using only the properties of pure solvent:

$$G_{SS} = RT \ln \left( \frac{RT}{p^\circ V_w} \right) \\ S_{SS} = - \left( \frac{\partial G_{SS}}{\partial T} \right)_p = R \left( \ln \left( \frac{RT}{p^\circ V_w} \right) + 1 - \alpha_w T \right) \quad (21)$$

where  $p^\circ = 0.1$  MPa and  $V_w$  and  $\alpha_w$  are the molar volume and the coefficient of thermal expansion of water, respectively.

The sum of the three integrals on the right-hand side of Eq. (19) is calculated from the high-temperature hydration model (Sedlbauer–O'Connell–Wood, SOCW) proposed by Sedlbauer et al. [16]. Since the integration of the standard heat capacity equation is complex within this model it is more convenient to rearrange Eq. (19) as follows:

$$\Delta G_{hyd} [T, p] = \Delta G_{hyd}^\circ [T_{ref}, p_{ref}] - (T - T_{ref}) \Delta S_{hyd}^\circ [T_{ref}, p_{ref}] \\ + \Delta G_{hyd}^{mod} [T, p] - (\Delta G_{hyd}^{mod} [T_{ref}, p_{ref}] \\ - (T - T_{ref}) \Delta S_{hyd}^{mod} [T_{ref}, p_{ref}]) \quad (22)$$

It is apparent that the sum of integrals is replaced by a combination of three terms (denoted by superscript mod) using the

**Table 2**  
Group contributions for calculating parameters of the  $T, p$  dependent (SOCW) model

Functional group	$a \times 10^3$ ( $\text{m}^3 \text{kg}^{-1} \text{mol}$ )	$b \times 10^4$ ( $\text{m}^3 \text{kg}^{-1} \text{mol}$ )	$c \times 10^6$ ( $\text{m}^3 \text{kg}^{-1} \text{mol}$ )	$d$	$e \times 10$ ( $\text{JK}^{-2} \text{mol}^{-1}$ )
C <sup>a</sup>	-34.6310	9.4034	-53.9212	-7.3260	-13.7921
CH <sup>a</sup>	-6.5437	1.8156	-16.9215	-0.9492	-3.9136
CH <sub>2</sub> <sup>a</sup>	-0.0244	0.7216	-8.9576	0.3416	-1.8264
CH <sub>3</sub> <sup>a</sup>	7.2778	-0.1571	-1.9499	1.4268	-0.0177
C=C <sup>a</sup>	-10.2988	-9.5352	-12.9835	11.4045	1.4871
H <sub>n</sub> <sup>a</sup>	2.8400	3.1911	9.2357	-3.1496	0.5847
c-CH <sup>a</sup>	-16.9864	4.8289	5.0487	-3.3563	-0.9028
c-CH <sub>2</sub> <sup>a</sup>	3.0612	0.1108	-7.6472	0.7839	-1.2200
C <sub>ar</sub> <sup>a</sup>	-9.1549	2.2106	-21.3460	-1.3723	-4.9993
CH <sub>ar</sub> <sup>a</sup>	0.6924	0.5168	-5.0903	0.3337	-1.0754
CH <sub>4</sub> <sup>b</sup>	3.90203	2.09843	-2.4163	0	-0.746493
CO <sub>2</sub> <sup>b</sup>	3.15041	1.5963	-9.65805	0.407478	-1.90856
H <sub>2</sub> S <sup>b</sup>	1.36697	1.69674	-12.8815	0.443516	-2.81635

<sup>a</sup> Group contributions for hydrocarbons reported by Sedlbauer et al. [15].

<sup>b</sup> Parameters for individual compounds determined in this work.

expressions for the Gibbs energy and entropy of hydration from the high-temperature model.

The equation for the standard molar volume of an aqueous solute is the basic relationship of the SOCW model:

$$V_s^\circ = RT\kappa_w + d(V_w - RT\kappa_w) + RT\kappa_w\rho_w \left( a + b(\exp[\vartheta\rho_w] - 1) + c \exp\left[\frac{\theta}{T}\right] + \delta(\exp[\lambda\rho_w] - 1) \right) \quad (23)$$

where  $\nu = 0.005 \text{ m}^3/\text{kg}$ ,  $\theta = 1500 \text{ K}$  and  $\lambda = -0.01 \text{ m}^3/\text{kg}$  are the pre-determined general constants valid for all solutes. The solute specific adjustable parameters are  $a$ ,  $b$ ,  $c$  and  $d$ , while  $\delta = 0.35a$  holds for all nonelectrolytes. This equation is in fact modeling a series of perturbation effects due to: (i) insertion of a material point into water solvent ( $V_{SS} = RT\kappa_w$ ), (ii) growing it to a “water-like” molecule with size adjusted to mimic the intrinsic volume of a solute ( $d(V_w - RT\kappa_w)$ ), and (iii) then changing its potential field from solvent–solvent to solute–solvent interaction. This last contribution is modeled by the third term on the right-hand side of Eq. (23) that is purely empirical. This equation has correct limiting behavior, i.e. it reduces to the virial equation truncated after the second virial coefficient at low densities and diverges at the critical point of water [16].

Since the process of hydration is defined as an isothermal transfer of a solute molecule from an ideal gas state at  $p_{\text{ref}} = 0.1 \text{ MPa}$  to aqueous solution at a pressure  $p$  it is possible to write the Gibbs energy of hydration as

$$\Delta G_{\text{hyd}}^{\circ \text{mod}} = \int_{p_{\text{ref}}}^0 RT d \ln p + \int_0^p V_s^\circ dp + \Delta G_{\text{hyd}}^{\circ \text{cor}} \quad (24)$$

**Table 3**  
Survey of the database of experimental values

Compound type	Total number of experimental values (number of compounds)			
	$K_H$	$\Delta H_{\text{hyd}}^\circ$	$C_{p,s}^\circ$	$V_s^\circ$
Alkanes ( $N_C > 1$ )	295 (8)	63 (6)	1 (1)	5 (1)
Alkenes	291 (5)	6 (3)	3 (3)	–
Cycloalkanes	27 (3)	12 (2)	–	6 (1)
Alkylbenzenes	445 (7)	56 (6)	16 (2)	72 (6)
Alcohols	–	–	44 (16)	286 (22)
Total	1058 (23)	137 (17)	64 (22)	369 (30)
CH <sub>4</sub>	45	17	6	18
CO <sub>2</sub>	73	1	7	17
H <sub>2</sub> S	27	1	9	19

where  $V_s^\circ$  is expressed from Eq. (23). An additional empirical correction term  $\Delta G_{\text{hyd}}^{\circ \text{cor}}$  is needed at subcritical conditions since the simple volumetric Eq. (23) is not sufficient for describing quantitatively the integration across the vapor–liquid saturation line. This correction is defined on the heat capacity level and for nonelectrolytes has the form

$$-\left(\frac{\partial^2 \Delta G_{\text{hyd}}^{\circ \text{cor}}}{\partial T^2}\right)_p = \left(\frac{\partial \Delta S_{\text{hyd}}^{\circ \text{cor}}}{\partial T}\right)_p = \frac{\Delta C_{p,\text{hyd}}^{\circ \text{cor}}}{T} = \frac{e(T - T_c)^2}{T(T - 228)}, \quad (25)$$

$T < T_c$

where  $e$  is an additional adjustable parameter. Contribution of the correction term is decreasing with increasing temperature and it vanishes at the critical temperature of solvent ( $\Delta C_{p,\text{hyd}}^{\circ \text{cor}} = \Delta H_{\text{hyd}}^{\circ \text{cor}} = \Delta G_{p,\text{hyd}}^{\circ \text{cor}} = 0$ ,  $T \geq T_c$ ) thus providing integration constant for Eq. (24). Once the expression for  $\Delta G_{\text{hyd}}^{\circ \text{mod}}$  is available, the model equation for the entropy of hydration also required in Eq. (22) is simply obtained as

$$\Delta S_{\text{hyd}}^{\circ \text{mod}} = \left(\frac{\partial \Delta G_{\text{hyd}}^{\circ \text{mod}}}{\partial T}\right)_p \quad (26)$$

Full expressions for  $\Delta G_{\text{hyd}}^{\circ \text{mod}}$ ,  $\Delta S_{\text{hyd}}^{\circ \text{mod}}$  and other thermodynamic functions within the SOCW model can be found in Appendix A.

The five parameters  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$  of the temperature and pressure dependent model are obtained for hydrocarbons ( $N_C > 1$ ) from the group contributions tabulated in Table 2. Each parameter for the solute of interest is calculated as a linear combination of the

appropriate parameters of constituting groups, e.g.

$$a = \sum_{i=1}^N n_i a_i \quad (27)$$

where  $N$  is the total number of structural groups present in the given solute,  $n_i$  is the number of occurrences of each specific group, and  $a_i$  stands for the  $a$  parameter of the  $i$ th group taken from Table 2. The molecular fragments are defined in an identical way as the group contributions used for the calculation at the reference conditions  $T_{\text{ref}}$ ,  $p_{\text{ref}}$  (Table 1), the proximity effect  $I(\text{C}-\text{C})$  on aromatic ring is not, however, considered. The material point contribution (Eq. (21)) that is temperature dependent appears explicitly in Eq. (24) and therefore it is not listed in Table 2. The group contributions for  $\text{C}_2$  and higher hydrocarbons were taken over from the article by Sedlbauer et al. [15]. For illustration Table 3 gives the number of data points and compounds that were considered per class of hydrocarbons when determining the group contributions by simultaneous correlation of the experimental Henry's law constants and their derivative properties. A certain amount of data on derivative properties ( $\Delta C_{p,\text{hyd}}^\circ$ ,  $V_s^\circ$ ) for alcohols were also included that was helpful for increasing numerical stability of the group contribution determination for the less frequent functional groups (for more information see reference [15]).

Using analogous simultaneous correlation procedure like for hydrocarbons, the parameters were newly determined for  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . These three aqueous solutes belong to experimentally well-studied systems with data available for most properties characterizing hydration at elevated temperatures and extending in the case of  $V_s^\circ$  and  $\Delta C_{p,\text{hyd}}^\circ$  to supercritical conditions. When establishing the parameters of the SOCW model we have used the Henry's law constants along the saturation line of water determined from the gas solubility data reported in a variety of literature sources listed in Table 4. Major sources of derivative properties were the papers by Hnedkovsky and Wood [38] and by Hnedkovsky et al. [42], reporting the standard heat capacities obtained by the Picker-type flow calorimetry and the standard volumes from measurements by vibrating tube densimetry, respectively. These data were included for the three gases up to 623 K and 35 MPa in the case of volumes and at one isobar (28 MPa) for the heat capacities. The enthalpies of hydration are available for  $\text{CH}_4$  at temperatures to 323 K, originating from the unique measurements carried out by the groups of Gill et al. [34,35,37] and Wadsö and co-workers [36]. Only one enthalpic data point at 298 K is, however, reported for  $\text{CO}_2$  and  $\text{H}_2\text{S}$ . The properties of the solutes in the ideal gas phase, needed for converting  $C_{p,s}^\circ$  to  $\Delta C_{p,\text{hyd}}^\circ$ , were taken from the JANAF Thermochemical Tables [40]. Overall numbers of data points relating to individual thermodynamic properties are presented for the three gases in Table 3 and a detailed survey is given in Table 4.

The parameters of the SOCW model were obtained by the simultaneous correlation of the Henry's law constants and the data on the three derivative properties using the weighted least squares procedure with weights reflecting the expected experimental uncertainties. They were estimated at 2% for  $K_{\text{H}}$  of  $\text{CH}_4$  and at 3% for  $\text{CO}_2$  and  $\text{H}_2\text{S}$ , based on the root-mean-square deviations of the data from the correlation of Fernandez-Prini et al. [17]. For the derivative properties the expected errors were set between 1% and 3% for  $\Delta H_{\text{hyd}}^\circ$  and  $V_s^\circ$ , and between 3% and 5% for  $\Delta C_{p,\text{hyd}}^\circ$ , according to the error estimates in the original data sources and the fact that the relative error increases with the temperature. The objective minimized function  $O$  was defined as

$$O = \sum_{j=1}^4 \sum_{i=1}^{n_j} \left[ \frac{X_i^{\text{mod},j} - X_i^{\text{exp},j}}{\sigma X_i^j} \right]^2 \quad (28)$$

**Table 4**

Survey of data sources to determine the parameters of the SOCW model

Literature sources in chronological order	Prop.	$N_{\text{points}}$	$T$ (K)	$p$ (MPa)
<b><math>\text{CH}_4</math></b>				
Michels et al. [28]	$K_{\text{H}}$	4	323–423	sat
Culberson and McKetta [29]	$K_{\text{H}}$	6	298–444	sat
Sultanov et al. [30]	$K_{\text{H}}$	5	423–633	sat
Rettich et al. [31]	$K_{\text{H}}$	16	275–328	sat
Cramer [32]	$K_{\text{H}}$	7	297–518	sat
Crovetto et al. [33]	$K_{\text{H}}$	7	334–554	sat
Dec and Gill [34]	$H$	1	298	0.1
Dec and Gill [35]	$H$	2	288–308	0.1
Oloffson et al. [36]	$H$	3	288–308	0.1
Naghibi et al. [37]	$H$	11	273–323	0.1
Hnedkovsky and Wood [38]	$C_p$	6	303–623	28
Tiepel and Gubbins [39]	$V$	1	298	0.1
Moore et al. [41]	$V$	1	298	0.1
Hnedkovsky et al. [42]	$V$	16	298–623	28–35
<b><math>\text{CO}_2</math></b>				
Wiebe and Gaddy [43]	$K_{\text{H}}$	3	323–373	sat
Wiebe and Gaddy [44]	$K_{\text{H}}$	3	304–313	sat
Morrison and Billet [45]	$K_{\text{H}}$	19	286–347	sat
Malinin [46]	$K_{\text{H}}$	4	473–603	sat
Ellis and Golding [47]	$K_{\text{H}}$	9	450–582	sat
Takenouchi and Kennedy [48]	$K_{\text{H}}$	9	423–623	sat
Murray and Riley [49]	$K_{\text{H}}$	8	274–308	sat
Cramer [32]	$K_{\text{H}}$	3	306–405	sat
Shagiakhmetov and Tarzimanov [50]	$K_{\text{H}}$	2	323–373	sat
Müller et al. [51]	$K_{\text{H}}$	6	373–473	sat
Nishswander et al. [52]	$K_{\text{H}}$	2	353–471	sat
Crovetto and Wood [53]	$K_{\text{H}}$	3	623–643	sat
Bamberger et al. [54]	$K_{\text{H}}$	2	333–353	sat
Berg and Vanderzee [55]	$H$	1	298	0.1
Barbero et al. [56]	$C_p$	1	298	0.1
Hnedkovsky and Wood [38]	$C_p$	6	304–623	28
Moore et al. [41]	$V$	1	298	0.1
Hnedkovsky et al. [42]	$V$	16	298–623	20–35
<b><math>\text{H}_2\text{S}</math></b>				
Selleck et al. [57]	$K_{\text{H}}$	3	377–444	sat
Lee and Mather [58]	$K_{\text{H}}$	11	283–453	sat
Gillespie and Wilson [59]	$K_{\text{H}}$	3	422–533	sat
Carroll and Mather [60]	$K_{\text{H}}$	10	273–333	sat
Cox et al. [61]	$H$	1	298	0.1
Barbero et al. [62]	$C_p$	3	283–313	0.1
Hnedkovsky and Wood [38]	$C_p$	6	304–623	28
Barbero et al. [56]	$V$	3	283–313	0.1
Hnedkovsky et al. [42]	$V$	16	304–623	20–35

where  $X^j$  and  $\sigma X^j$  stand for  $K_{\text{H}}$ ,  $\Delta H_{\text{hyd}}^\circ$ ,  $\Delta C_{p,\text{hyd}}^\circ$ ,  $V_s^\circ$  and their errors, respectively, and  $n_j$  are the numbers of data points for the four properties. Explicit equations for the thermodynamic functions resulting from the SOCW model (denoted with the upper index mod in Eqs. (24)–(26)) are presented in Appendix A. The adjustable parameters of the SOCW model obtained for aqueous  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2\text{S}$  are summarized in Table 2 along with parameters for the hydrocarbon functional groups evaluated earlier [15]. A quantitative comparison is made in Table 5 between the data calculated for the three gases from the SOCW model and the values resulting from the other two recently published models valid along the saturation line of water [17,63]. It is apparent that the agreement among the models at  $p_{\text{w}}^{\text{sat}}$  is quantitative for  $\text{CH}_4$  and  $\text{CO}_2$ . Some differences are observed for  $\text{H}_2\text{S}$  due to higher uncertainty in the Henry's law constants that are not quite consistent at elevated temperatures with the  $\Delta C_{p,\text{hyd}}^\circ$  and  $V_s^\circ$  data.

Figs. 1–4 illustrate the changes in the Henry's law constant with the structure of the solute and with temperature and pressure up to 623 K and 80 MPa for hydrocarbons having eight carbon atoms and for the three gases. First the results of the calculation for  $K_{\text{H}}$  from

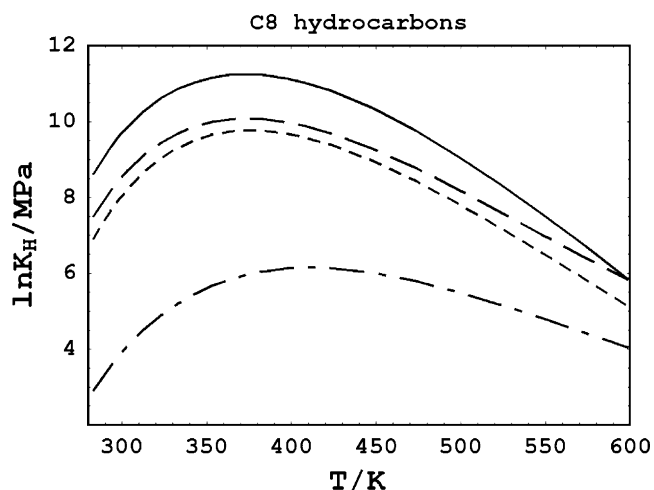


Fig. 1. The Henry's law constants calculated along the saturation line of water from the group contribution model [15] for  $C_8$  hydrocarbons: *n*-octane (full), 1-octene (long-dashed), ethylcyclohexane (short-dashed) and ethylbenzene (dashed-dot line).

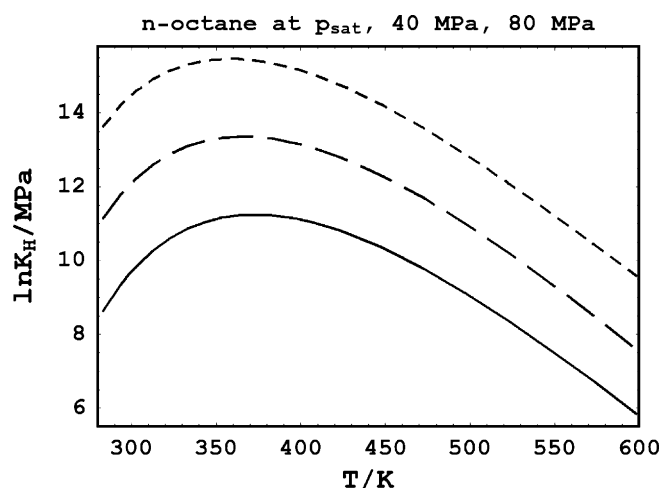


Fig. 2. The Henry's law constants for *n*-octane calculated as a function of temperature along the saturation line of water (full) and at pressures of 40 MPa (long-dashed) and 80 MPa (short-dashed line).

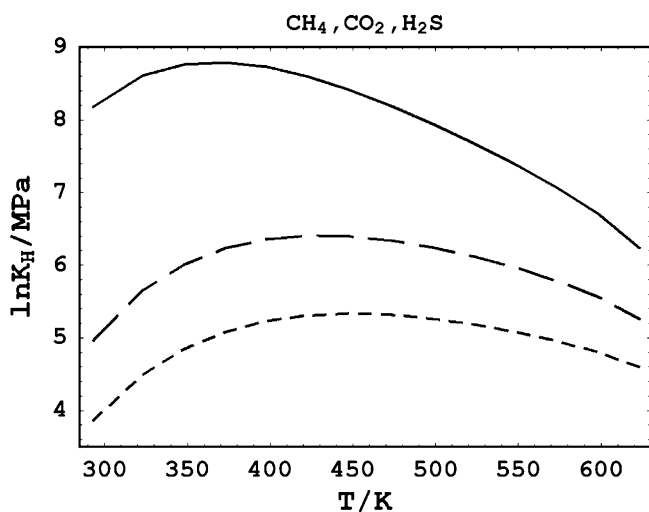


Fig. 3. The Henry's law constants calculated along the saturation line of water from the presented model for methane (full), carbon dioxide (long-dashed) and hydrogen sulfide (short-dashed line).

Table 5

Henry's law constants calculated along the saturation line of water and at elevated pressures from the presented model for octane, methane, carbon dioxide and hydrogen sulfide

$p$ (MPa)	$\ln K_H$ at 298 K	$\ln K_H$ at 373 K	$\ln K_H$ at 473 K	$\ln K_H$ at 573 K
<i>n</i> -Octane				
$p_{sat}$	9.60	11.25	9.77	6.73
10	10.21	11.78	10.20	6.82
40	12.02	13.36	11.69	8.51
80	14.42	15.43	13.58	10.45
CH <sub>4</sub>				
$p_{sat}$	8.28	8.79	8.20	7.07
Ref. [17] at $p_{sat}$	8.28	8.77	8.20	7.09
Ref. [63] at $p_{sat}$	8.33	8.82	8.27	7.12
10	8.43	8.92	8.32	7.10
40	8.88	9.32	8.73	7.70
80	9.49	9.83	9.24	8.30
CO <sub>2</sub>				
$p_{sat}$	5.11	6.23	6.34	5.78
Ref. [17] at $p_{sat}$	5.11	6.23	6.35	5.81
Ref. [63] at $p_{sat}$	5.08	6.27	6.50	5.98
10	5.25	6.36	6.45	5.81
40	5.66	6.72	6.82	6.32
80	6.22	7.20	7.28	6.84
H <sub>2</sub> S				
$p_{sat}$	3.99	5.08	5.32	4.96
Ref. [17] at $p_{sat}$	3.99	5.03	5.33	5.00
Ref. [63] at $p_{sat}$	3.99	5.08	5.23	4.78
10	4.13	5.21	5.42	4.98
40	4.55	5.58	5.79	5.45
80	5.12	6.07	6.25	5.95

Comparison for CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S at  $p_{sat}$  with the values (in italics) calculated from the formulations of Fernandez-Prini et al. [17] and of Akinfiev and Diamond [63].

the group contributions are presented along the saturation line of water for four different  $C_8$  hydrocarbons (Fig. 1) and for *n*-octane as a function of temperature and pressure (Fig. 2). Second, analogous plots are in Figs. 3 and 4 for the aqueous gases.

Table 6 listing the ratios  $K_H(p)/K_H(p_w^{sat})$  for octane, methane, carbon dioxide and hydrogen sulfide at three pressures and four temperatures summarizes quantitatively the change of the Henry's law constant with pressure for the four solutes. It is apparent from Eq. (9) that the standard molar volume of a solute plays a major role in determining this factor. Thus, the pressure effect is much stronger for octane than for the three gaseous solutes due to

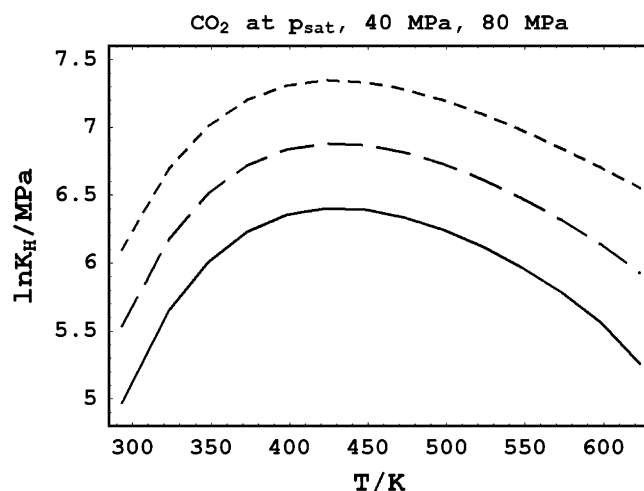


Fig. 4. The Henry's law constants for carbon dioxide calculated as a function of temperature along the saturation line of water (full) and at pressures of 40 MPa (long-dashed) and 80 MPa (short-dashed line).

**Table 6**  
Ratios  $K_H(p)/K_H(p_w^{\text{sat}})$  for octane, methane, carbon dioxide and hydrogen sulfide

$K_H(p)/K_H(p_w^{\text{sat}})$	323 K ( $p_w^{\text{sat}} \approx 0.1$ MPa)			373 K ( $p_w^{\text{sat}} \approx 0.1$ MPa)			473 K ( $p_w^{\text{sat}} \approx 1.6$ MPa)			573 K ( $p_w^{\text{sat}} \approx 8.7$ MPa)		
	10 MPa	50 MPa	100 MPa	10 MPa	50 MPa	100 MPa	10 MPa	50 MPa	100 MPa	10 MPa	50 MPa	100 MPa
Octane	1.8	17	289	1.7	14	181	1.5	11	114	1.1	10	101
CH <sub>4</sub>	1.2	2.0	4.0	1.1	1.9	3.6	1.1	1.9	3.6	1.0	2.2	4.5
CO <sub>2</sub>	1.1	1.9	3.7	1.1	1.8	3.3	1.1	1.8	3.2	1.0	2.0	3.6
H <sub>2</sub> S	1.1	1.9	3.8	1.1	1.8	3.4	1.1	1.8	3.2	1.0	1.9	3.4

the difference in the  $V_s^\circ$  values (about 100 cm<sup>3</sup>/mol for C<sub>8</sub>H<sub>18</sub> and close to 35 cm<sup>3</sup>/mol for the three gases at 298.15 K). At superambient conditions, the standard molar volume increases substantially with increasing temperature and decreases with pressure, it scales approximately with the compressibility of water and diverges at the critical point of the solvent. For the pressures dependence of  $K_H$  the increase in volume at high temperatures is, however, partly compensated by dividing with temperature in Eq. (9). Therefore, the relative pressure effect on  $K_H$  does not change much with temperature at conditions remote from the critical point of water.

#### 4. Software package for calculating the Henry's law constant and related distribution coefficients

As apparent from the equations listed in Appendix A, the applied model is rather complex and requires the use of a fundamental equation of state allowing calculation of the thermodynamic properties of water. A programming effort would be necessary before using the method. In addition, the Henry's law constant or another related coefficients are required in varying pressure and concentration units depending on the users and erroneous conversions often lead to confusion. For that reason we have prepared a computer code with a user-friendly interface allowing generation of the Henry's law constants from the model as a function of temperature and pressure in several types of units as well as the calculation of other two coefficients defined by Eqs. (13) and (16) that are closely related to the Henry's law constant. Using the group contributions listed in Tables 1 and 2 the estimations can be performed for normal and branched alkanes and alkenes C<sub>2</sub> to C<sub>12</sub> and for the monocyclic saturated or aromatic hydrocarbons (typically for C<sub>6</sub> ring compounds) with one or several alkyl groups up to C<sub>8</sub>. In addition, the software uses specific parameters for methane, carbon dioxide and hydrogen sulfide. The calculations can be made at temperatures up to 623 K either along the saturation line of water or at distinct pairs of temperature and pressure ( $p_w^{\text{sat}} < p < 100$  MPa). When running the program the user chooses from several options allowing the calculation of one of the following parameters: the Henry's law constant  $K_H$  defined in terms of the mol fraction (Eq. (1)), its modifications  $K_{Hm}$  and  $K_{Hc}$  (Eq. (6)) using as concentration variables molality (mol/kg) or molarity (mol/m<sup>3</sup>), respectively, the air–water partition coefficient  $K_{aw}$  (Eq. (16)) and the vapor–liquid distribution constant (relative volatility)  $K_d$  (Eq. (13)). The air–water partition coefficient is used for expressing the partition of a solute between air and water at near-ambient conditions and the calculation is made therefore only at pressures below 0.5 MPa. Similarly due to its definition the vapor–liquid distribution constant can be calculated solely along the saturation line of water. The five coefficients are in the code interconnected by the limiting conversion expressions as follows

$$K_H = \frac{K_{Hm}}{m_o M_w} = \frac{K_{Hc} \rho_w}{c_o M_w} = \frac{K_{aw} RT \rho_w}{M_w} = \frac{K_d}{p_{\text{sat},w}} \quad (29)$$

where the meaning of individual symbols was explained above (see Eqs. (6), (14) and (17)). Compared to Eq. (14) it is apparent that the saturation pressure of water is used in the conversion (Eq. (29))

instead of fugacity. This simplifying assumption of an ideal gas behavior of the vapor phase can lead to an increase of uncertainty in  $K_d$  at high temperatures where the fugacity coefficient of water can differ significantly from unity.

The code is available on request as shareware for non-commercial users from academia (contacts: [vladimir.majer@univ-bpclermont.fr](mailto:vladimir.majer@univ-bpclermont.fr) and [josef.sedlbauer@tul.cz](mailto:josef.sedlbauer@tul.cz)). The preparation of input files, the operation of the code and a few illustrative examples of the input and output files are described in the README document that is distributed along with the software.

#### List of symbols

$c$	molarity
$C$	heat capacity
$f$	fugacity
$G$	Gibbs energy
$H$	enthalpy
$K_{aw}$	air–water partition coefficient
$K_d$	vapor–liquid distribution coefficient
$K_H$	Henry's law constant
$m$	molality
$M$	molar mass
$N$	total number of functional groups in a molecule
$O$	minimized objective function
$p$	pressure
$R$	universal gas constant
$S$	entropy
$SS$	intrinsic value
$T$	thermodynamic temperature
$V$	volume
$x$	molar fraction liquid phase
$\bar{X}$	partial molar property ( $X = G, H, S, V, C$ )
$y$	molar fraction gaseous phase

#### Greek letters

$\alpha$	expansivity
$\gamma$	activity coefficient change
$\varphi$	fugacity coefficient
$\kappa$	compressibility
$\rho$	density
$\sigma$	absolute error

#### Superscripts

a	air phase
calc	calculated
cor	correction term
exp	experimental
g	gas phase
H	property compatible with the Henry's law
ig	ideal gas
l	liquid phase
mod	high-temperature model
R	property compatible with the Raoult's law
sat	saturation
sol	solubility



w	aqueous phase
°	standard state of infinite dilution
∞	limiting value
•	pure compound

#### Subscripts

c	relating to molarity
hyd	hydration
m	relating to molality
o	unit value
ref	reference state
s	solute
sol	dissolution
SS	intrinsic value
w	water
x	relating to molar fraction

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#### Appendix A. Thermodynamic functions of hydration from the SOCW model

The Gibbs energy of hydration is expressed in the SOCW model [16] as:

$$\begin{aligned} \Delta G_{\text{hyd}}^{\circ} = & RT \ln \left[ \frac{\rho_w RT}{M_w p_{\text{ref}}} \right] + d \left( G_w - G_w^{\text{ig}} - RT \ln \left[ \frac{\rho_w RT}{M_w p_{\text{ref}}} \right] \right) \\ & + RT \left( \rho_w \left( a + c \exp \left[ \frac{\theta}{T} \right] - b - \delta \right) + \frac{b}{\vartheta} (\exp[\vartheta \rho_w] - 1) \right) \\ & + \frac{\delta}{\lambda} (\exp[\lambda \rho_w] - 1) + \Delta G_{\text{hyd}}^{\text{cor}} \end{aligned} \quad (\text{A.1})$$

Appropriate temperature derivations of  $\Delta G_{\text{hyd}}^{\circ}$  (see Eqs. (3), (7) and (8) in the main text) lead to other thermodynamic properties of hydration

$$\begin{aligned} \Delta H_{\text{hyd}}^{\circ} = & RT(T\alpha_w - 1) + d(H_w - H_w^{\text{ig}} - RT(T\alpha_w - 1)) \\ & + RT\theta c \exp \left[ \frac{\theta}{T} \right] \frac{\rho_w}{T} - RT^2 \left( \frac{\partial \rho_w}{\partial T} \right)_p (a + b(\exp[\vartheta \rho_w] - 1)) \\ & + c \exp \left[ \frac{\theta}{T} \right] + \delta(\exp[\lambda \rho_w] - 1) + \Delta H_{\text{hyd}}^{\text{cor}} \end{aligned} \quad (\text{A.2})$$

$$\Delta S_{\text{hyd}}^{\circ} = \frac{\Delta H_{\text{hyd}}^{\circ} - \Delta G_{\text{hyd}}^{\circ}}{T} \quad (\text{A.3})$$

$$\begin{aligned} \Delta C_{p,\text{hyd}}^{\circ} = & \left( 2RT\alpha_w + RT^2 \left( \frac{\partial \alpha_w}{\partial T} \right)_p - R \right) \\ & + d \left( C_{p,w} - C_{p,w}^{\text{ig}} - \left( 2RT\alpha_w + RT^2 \left( \frac{\partial \alpha_w}{\partial T} \right)_p - R \right) \right) \\ & - T \left( 2R \left( \frac{\partial \rho_w}{\partial T} \right)_p (a + b(\exp[\vartheta \rho_w] - 1) + c \exp \left[ \frac{\theta}{T} \right] \right) \end{aligned}$$

$$\begin{aligned} & + \delta(\exp[\lambda \rho_w] - 1) - c \exp \left[ \frac{\theta}{T} \right] \frac{\theta}{T} + Rc \exp \left[ \frac{\theta}{T} \right] \theta^2 \frac{\rho_w}{T^3} \\ & + RT \left( \frac{\partial \rho_w}{\partial T} \right)_p^2 (\vartheta b \exp[\vartheta \rho_w] + \lambda \delta \exp[\lambda \rho_w]) \\ & + RT \left( \frac{\partial^2 \rho_w}{\partial T^2} \right)_p \left( a + b(\exp[\vartheta \rho_w] - 1) + c \exp \left[ \frac{\theta}{T} \right] \right) \\ & + \delta(\exp[\lambda \rho_w] - 1) + \Delta C_{p,\text{hyd}}^{\text{cor}} \end{aligned} \quad (\text{A.4})$$

where  $G_w$ ,  $H_w$ ,  $C_{p,w}$  are the molar Gibbs energy, enthalpy and heat capacity of water,  $G_w^{\text{ig}}$ ,  $H_w^{\text{ig}}$ ,  $C_{p,w}^{\text{ig}}$  are the same properties of water in an ideal gas standard state and  $\alpha_w = -1/\rho_w(\partial \rho_w/\partial T)_p$  is the isobaric coefficient of thermal expansion. Thermodynamic properties of water were obtained in this study from the equation of state by Hill [64]. The correction terms are expressed by an empirical function with one additional adjustable parameter,  $e$

$$\Delta C_{p,\text{hyd}}^{\text{cor}} = \frac{e(T - T_c)^2}{T - \Phi} \quad (\text{A.5})$$

$$\Delta S_{\text{hyd}}^{\text{cor}} = e \left( T - T_c - \frac{T_c^2}{\Phi} \ln \left[ \frac{T}{T_c} \right] + \frac{(T_c - \Phi)^2}{\Phi} \ln \left[ \frac{T - \Phi}{T_c - \Phi} \right] \right) \quad (\text{A.6})$$

$$\begin{aligned} \Delta H_{\text{hyd}}^{\text{cor}} = & e \left( (2T_c - \Phi)(T_c - T) + \frac{1}{2}(T^2 - T_c^2) \right. \\ & \left. + (T_c - \Phi)^2 \ln \left[ \frac{T - \Phi}{T_c - \Phi} \right] \right) \end{aligned} \quad (\text{A.7})$$

$$\Delta G_{\text{hyd}}^{\text{cor}} = (\Delta H_{\text{hyd}}^{\text{cor}} - T \Delta S_{\text{hyd}}^{\text{cor}}) \quad (\text{A.8})$$

where  $\Phi = 228$  K is a general constant. Correction terms defined by Eqs. (A.5)–(A.8) apply only at temperatures below the critical temperature of water  $T_c = 647.1$  K and are by definition equal to zero at  $T_c \geq 0$ . All thermodynamic properties that appear in the above equations should be applied in their basic SI units when using parameters from Table 2 of the main text.

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