



# Solubility of Gases in Liquids. 23: High-Precision Determination of Henry's Law Constants of Propane Dissolved in Liquid Water from $T = 278$ K to $T = 318$ K

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Received: 15 February 2023 / Accepted: 30 March 2023 / Published online: 29 May 2023  
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## Abstract

The solubility of propane ( $C_3H_8$ , component 2) in pure liquid water ( $H_2O$ , component 1) was determined at a total pressure of about 100 kPa from about  $T = 278$  K to  $T = 318$  K using an analytical method characterized by an imprecision of about  $\pm 0.1\%$  or less. The measurements were made with a Benson-Krause-type apparatus at roughly 5 K intervals. From the experimental results, Henry's law constants  $h_{2,1}(T, P_{\sigma,1})$ , also known as Henry fugacities, at the vapor pressure  $P_{\sigma,1}(T)$  of water, as well as the Ostwald coefficient  $L_{2,1}^\infty(T, P_{\sigma,1})$  at infinite dilution are rigorously obtained. The temperature dependence is accounted for by a three-constant Benson-Krause equation, i.e., by fitting  $\ln [h_{2,1}(T, P_{\sigma,1})/kPa]$  to a power series in  $1/T$ . Subsequently, the partial molar enthalpy changes on solution  $\Delta H_2^\infty$  of propane in water, and the partial molar heat capacity changes on solution  $\Delta C_{p,2}^\infty$ , are reported (van 't Hoff analysis) and compared with calorimetrically determined quantities: agreement is highly satisfactory. We believe that our new values for the Henry fugacity and the Ostwald coefficient of propane dissolved in liquid water are the most reliable ones to date.

**Keywords** Solubility of propane in water · Henry fugacity (Henry's law constant) · Ostwald coefficient · van 't Hoff analysis · Partial molar enthalpy changes on solution · Partial molar heat capacity changes on solution

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Communicated in part by Emmerich Wilhelm at the THERMO International 2006 (61st CALCON + 19th ICCT + 16th STP) in Boulder, Colorado, USA, July 30–August 4, 2006.

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## 1 Introduction

The study of the solubility of gases in liquids and of the thermodynamic properties of such solutions is of considerable practical importance in surprisingly diverse areas of the pure and applied sciences [1–5]. For instance, reliable gas solubility data are often needed in geochemistry (including petroleum reservoir production engineering), environmental science (pollution control), biomedical technology and chemical process design. The latter area includes enhanced oil recovery, natural-gas and synthetic-gas purification (gas sweetening), wastewater treatment and so forth. Note that propane ( $C_3H_8$ ) is an important constituent of liquified petroleum gas, a major fuel in its own right, and is used as a starting material in manufacturing. In addition, gas solubility studies (dilute solutions in general) have contributed decisively to the development of the physical chemistry of solutions [6–11]. When the focus is on *water* as solvent [12–19], we note that:

- Water is the most abundant substance on the surface of the earth (a rocky planet).
- Because of the earth’s size and its orbit within the so-called habitable zone of the solar system [18], water is the only substance that occurs naturally in all three states of matter, which fact is prerequisite for the emergence of life [20–26].
- Water sustains life as we know it: it is important for the structure, the stability, and the function of biomolecules [27–36]; in fact, it may no longer be regarded as being a mere medium in which bioprocesses occur, but as suggested by Ball [37], rather as an indispensable *active* matrix, a “biomolecule” itself.

Studies of aqueous solutions of simple nonpolar substances, say, of the rare gases [38, 39], nitrogen and oxygen [40–45] and of simple hydrocarbons [46], hold a prominent position in biophysics. In particular, the latter systems provide bio-relevant information on hydrophobic effects [12, 47, 48] that have long been recognized to be of importance in a wide variety of biological processes, such as the formation and stability of proteins, nucleic acids and cell membranes. Considering the wide scope of the field, the corresponding vast literature is not surprising: Refs. [12, 47–75] list a few classic works as well as selected recent ones.

A critical evaluation of the literature data available through 1983 on the solubility of propane (component 2) in liquid water (component 1) was prepared by Battino [76] (see also Ref. [77]). Only the data presented in six of the thirteen papers cited in that review were used to prepare a smoothing equation that expresses the mole fraction solubility  $x_2$  of propane dissolved in water, at a partial pressure  $P_2$  of the gas of 101.325 kPa (= 1 atm). For additional experimental data see Refs. [78–80]. The final smoothing equation selected for the temperature range 273.15–348.15 K was a three-term version of the Clarke-Glew (CG) equation [81], that is identical with the Valentiner equation [82]. The standard deviation was about 2% in  $x_2$ . Smoothed mole fraction solubilities at 101.325 kPa partial pressure of propane and Ostwald coefficients at 5 K intervals were given in tabular form. For the sake of comparison with more recent results, using the approximation for the Henry fugacity (also known as Henry’s law constant)  $h_{2,1} \approx P_2/x_2$  we recast the smoothing equation into.

$$\ln \left( \frac{h_{2,1}}{\text{kPa}} \right) = 288.446821 - \frac{14434.5}{T/\text{K}} - 39.4740 \ln \left( \frac{T}{\text{K}} \right) \quad (1)$$

For a rigorous definition of  $h_{2,1}$  see Eq. 5 below.

As already indicated above, solubilities in water of light hydrocarbons and natural-gas components, such as CO<sub>2</sub> and H<sub>2</sub>S, are of great interest to petroleum engineers, though emphasis was/is placed on modeling via appropriate equations of state. More recent work on propane solubility in water has been reported by Carroll and Mather [83] who carefully reanalyzed the results obtained by Kobayashi and Katz [78], obtaining

$$\ln \left( \frac{h_{2,1}}{\text{kPa}} \right) = 552.65815 + 0.077514 \left( \frac{T}{\text{K}} \right) - \frac{21334.4}{T/\text{K}} - 85.84949 \ln \left( \frac{T}{\text{K}} \right) \quad (2)$$

These data were also used, for instance, by Dhima et al. [84] and Rezania et al. [85].

New solubility measurements in the liquid–vapor region have been obtained over a wide temperature range, that is, 277.62 K to 368.16 K, and from 0.357 MPa up to 3.915 MPa, by Chapoy et al. [86]. Their solubilities are well represented by.

$$\ln \left( \frac{h_{2,1}}{\text{kPa}} \right) = 552.64799 + 0.078453 \left( \frac{T}{\text{K}} \right) - \frac{21334.4}{T/\text{K}} - 85.89736 \ln \left( \frac{T}{\text{K}} \right) \quad (3)$$

with an average absolute deviation (AAD) of about 1.5%, which is somewhat better than Eq. 2 (AAD = 2.7%). Note that for the fluid propane–water system there exists the possibility of three phases: (I) a vapor phase, (II) an aqueous liquid phase, and (III) a liquid phase rich in propane, i.e., the system exhibits liquid–liquid immiscibility.

Additional solubilities at fairly low pressures (i.e., at about 1–2.6 MPa) of propane in water, and of several other hydrocarbons, have been obtained by Mokraoui et al. [87]. Like Eq. 2, over the temperature range 298–343 K (6 data points) the Henry fugacities were fitted with a simple three-term CG-equation:

$$\ln \left( \frac{h_{2,1}}{\text{kPa}} \right) = 196.767755 - \frac{10156.70}{T/\text{K}} - 25.90 \ln \left( \frac{T}{\text{K}} \right) \quad (4)$$

Evidently, in the extant literature, results on the solubility of propane in water are quite scattered, and the amount of reliable experimental data is rather limited. In fact, Battino [76] has already suggested caution in the use of Eq. 1. In this paper we present our results on the solubility of propane in pure liquid water at pressures of about 100 kPa, and over the temperature range 278–318 K at roughly 5 K intervals. First, the experimental method is outlined briefly. It is based on the apparatus constructed by Benson and Krause (BK) [40, 42]. The high-precision technique we use since 1981 [46] profits from the excellent, novel equilibration technique developed by Benson and Krause [42], a very accurate volumetric measurement system [46], and thermodynamically rigorous data reduction [3, 4, 46] that will be presented concisely. This is followed by the presentation of the results, including derived caloric quantities pertaining to the solution process that were obtained via van't Hoff analysis [3, 4, 88, 89].

## 2 Experimental

The propane used was Matheson research purity grade with a minimum mole fraction purity of 0.9997. The oxygen used for routine check measurements [43] was Matheson ultra-high purity grade with a minimum mole fraction purity of 0.9995. Water was first purified by reverse osmosis followed by distillation in an all-Pyrex and quartz glass still and passed

through a series of Illco-Way research model ion exchangers and a micropore filter. The purified water had a resistivity greater than  $5 \times 10^5 \Omega \cdot \text{m}$ .

Adequate degassing of the solvent is indispensable for all gas-solubility determinations. The degassing method used in this work has been described elsewhere [90]. It yields degassed water with the residual air mole fraction being less than  $1 \times 10^{-10}$ . The experimental gas solubility method is based on the apparatus constructed by Benson and Krause [40, 42]; additional details (in particular, the thermodynamic basis of our way of data reduction) are given by Rettich et al. [46]. The high-precision technique profits greatly from a very accurate *PVT* measurement system and the BK equilibration technique that assures saturation of water with gas. Under gravity, purified and degassed water (component 1) flows under its own vapor pressure into the evacuated equilibrator. After adding propane (component 2) the equilibrator is sealed and placed in a large water bath controlled to  $\pm 0.003 \text{ K}$  for the duration of the experimental runs, that lasted between 16 and 48 h. A calibrated Leeds and Northrup Co. knife-blade platinum resistance thermometer was used for temperature measurements: temperatures are reported on IPTS-68. For the small differences in the present temperature range between IPTS-68 and ITS-90 see Refs [91] and [92]; compared to the uncertainties of the experimental Henry fugacities (and derived quantities), the impact of these differences is negligible. While Benson et al. use a mercury manometer to determine pressures, we use a Ruska quartz Bourdon tube manometer (model XR38) which is periodically calibrated against our laboratory standard Ruska air-piston deadweight gauge (model 2465) with traceability of calibration to the National Institute of Standards and Technology (NIST).

All molar quantities are based on the relative atomic mass table of IUPAC, 1983 [93]. Specifically,  $A_r(\text{H}) = 1.00794$ ,  $A_r(\text{C}) = 12.011$ , and  $A_r(\text{O}) = 15.9994$ . For the molar gas constant a value of  $R = 8.31441 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$  was used [94]. Note, however, that with the Avogadro constant  $N_A = 6.02214076 \times 10^{23} \text{ mol}^{-1}$  and the Boltzmann constant  $k_B = 1.380649 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}$  now being defined exactly [95, 96], the molar gas constant is thus fixed at  $R = N_A k_B = 8.314462618... \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ .

Since the thermodynamic method used for data reduction has been previously described in detail [46], only a brief summary of the salient features will be given. At the temperature  $T$  and the vapor pressure  $P_{\sigma,1}(T)$  of pure liquid solvent (here water), the Henry fugacity (also known as Henry's law constant) of solute 2 (here subcritical propane) dissolved in liquid solvent 1 is given by the *limiting value* of the ratio of the fugacity  $f_2^L(T, P, x_2)$  of the solute in the liquid phase (superscript L) and its liquid-phase mole fraction at constant temperature  $T$  [3–5, 97]:

$$h_{2,1}(T, P_{\sigma,1}) = \lim_{\substack{x_2 \rightarrow 0 \\ P \rightarrow P_{\sigma,1}}} \left( \frac{f_2^L(T, P, x_2)}{x_2} \right) = \lim_{\substack{x_2 \rightarrow 0 \\ P \rightarrow P_{\sigma,1}}} \left( \frac{y_2 P \phi_2^V(T, P, y_2)}{x_2} \right), \text{ constant } T \quad (5)$$

Here,  $y_2$  is the mole fraction of the solute in the coexisting vapor phase (superscript V) at total pressure  $P$ , and  $\phi_2^V(T, P, y_2)$  is the corresponding vapor-phase fugacity coefficient of component 2 (propane). Given the experimental conditions of our measurements, that is, low pressures of about 100 kPa or below, and hence very small mole fraction solubilities ( $x_2 < 5 \times 10^{-5}$ ), within the limits of the experimental precision the exact limiting relation Eq. 5 may be advantageously recast into [39, 41, 43, 44, 46, 98]

$$h_{2,1}(T, P_{\sigma,1}) = \tilde{h}_{2,1}(T, P) Z^V(T, P, y_2) \phi_2^V(T, P, y_2) C_2^{-1} \quad (6)$$

In Eq. 6,  $\tilde{h}_{2,1}(T, P)$  denotes the so-called *uncorrected Henry fugacity* (*uncorrected* Henry's law constant) that contains *all* the primary experimentally determined quantities [46],  $Z^V(T, P, y_2) = PV^V/RT$  is the vapor-phase compression factor with  $V^V$  being the molar volume of the vapor phase, and  $C_2 = C_2(T, P)$  represents the Poynting correction term referring to the solute:

$$C_2(T, P) = \exp \left\{ \int_{P_{\sigma,1}}^P \frac{V_2^{L,\infty}(T, P)}{RT} dP \right\}, \quad (7)$$

$$\simeq \exp \left\{ \frac{(P - P_{\sigma,1})V_2^{L,\infty}(T, P_{\sigma,1})}{RT} \right\} \quad (8)$$

Here,  $V_2^{L,\infty}$  is the partial molar volume of the solute at infinite dilution in the liquid phase [99]. The approximation Eq. 8 will become increasingly unsatisfactory for large pressure ranges ( $P - P_{\sigma,1}$ ) and in the critical region.

We note that the total equilibrium pressure  $P$  at any experimental temperature does not show up explicitly in Eq. 6. It must be known, however, for evaluating  $Z^V(T, P, y_2)$ , the component fugacity coefficient  $\phi_2^V(T, P, y_2)$  of the solute, and the Poynting correction term  $C_2(T, P)$ . Total pressure  $P$  and vapor-phase mole fraction  $y_2$  were determined by a rapidly converging iterative procedure described in detail in Ref. [46].

For low to moderate pressures, *real-gas* behavior is conveniently described by a two-term volume-explicit virial equation of state. With  $B_{11}$ ,  $B_{22}$  and  $B_{12}$  denoting the second virial coefficients of pure components 1 (i.e. water vapor) and 2 (propane vapor) and the composition-independent second virial cross-coefficient, respectively, the compression factor  $Z^V(T, P, y_2)$  of a binary vapor-phase mixture is given by

$$\left. \begin{aligned} Z^V(T, P, y_2) &= PV^V/RT = 1 + \frac{B(T, y_2)}{RT}P, \\ B(T, y_2) &= y_1B_{11} + y_2B_{22} + y_1y_2\delta_{12}, \\ \delta_{12} &= 2B_{12} - (B_{11} + B_{22}), \end{aligned} \right\} \quad (9)$$

where  $B$  denotes the second virial coefficient of the vapor mixture, and  $y_1 + y_2 = 1$ . For the fugacity coefficient of the solute in a binary vapor mixture we obtain

$$\phi_2^V(T, P, y_2) = \exp \left[ \frac{P(B_{22} + y_1^2\delta_{12})}{RT} \right] \quad (10)$$

For the temperature range considered, second virial coefficients of pure water vapor,  $B_{11}$ , were taken from O'Connell [100]. Note that these values are in excellent accord with the more recent correlation of Harvey and Lemmon [101]. Second virial coefficients  $B_{22}$  of pure propane vapor, were obtained by fitting recommended values from Dymond and Smith [102] over the temperature range of interest; these values are in excellent accord with the newer correlation of Lemmon et al. [103]. The second virial cross-coefficients  $B_{12}$  were estimated via the generalized corresponding-states method of Tsonopoulos [104] using as binary interaction parameter  $k_{12} = 0.382$ . This choice yields  $B_{12}$ s that are slightly

**Table 1** Critical temperatures  $T_{c,i}$ , critical pressures  $P_{c,i}$ , critical molar volumes  $V_{c,i}$ , and acentric factors  $\omega_i$  of water ( $\text{H}_2\text{O}$ ,  $i=1$ ) and of propane ( $\text{C}_3\text{H}_8$ ,  $i=2$ ) [107]

	$T_{c,i}/\text{K}$	$P_{c,i}/\text{kPa}$	$10^6 V_{c,i}/(\text{m}^3 \cdot \text{mol}^{-1})$	$\omega_i$
water ( $i=1$ )	647.3	22048	56.0	0.344
propane ( $i=2$ )	369.8	4250	203.0	0.153

**Table 2** Second virial coefficients of pure water vapor<sup>a</sup>  $B_{11}$  and of pure propane vapor<sup>b</sup>  $B_{22}$ , and second virial cross-coefficients<sup>c</sup>  $B_{12}$  at selected temperatures  $T$ 

$T/\text{K}$	$B_{11}/(\text{cm}^3 \cdot \text{mol}^{-1})$	$B_{22}/(\text{cm}^3 \cdot \text{mol}^{-1})$	$B_{12}/(\text{cm}^3 \cdot \text{mol}^{-1})$
278.15	-1661	-448	-188
283.15	-1511	-430	-181
288.15	-1380	-415	-173
293.15	-1265	-400	-167
298.15	-1164	-384	-160
303.15	-1074	-370	-154
308.15	-995	-356	-148
313.15	-925	-346	-143
318.15	-860	-332	-137

<sup>a</sup>Ref. [100]<sup>b</sup>Smoothed values, from fit of data recommended in Ref. [102]<sup>c</sup>Calculated via the generalized corresponding-states method of Tsounopoulos [104]

more negative than those determined by Wormald and Lancaster [105]: for instance, at 300 K our estimate is about  $30 \text{ cm}^3/\text{mol}$  more negative than their value (cf. their Fig. 4), thereby reflecting the considerably more negative second virial cross-coefficients reported by Skripka [106]. Table 1 provides ancillary physical property data [107], that is, critical temperature  $T_c$ , critical pressure  $P_c$ , critical molar volume  $V_c$ , and acentric factor  $\omega_1$  of water and  $\omega_2$  of propane. Table 2 contains the second virial coefficients of pure water vapor and pure propane vapor, and second virial cross-coefficients for the binary vapor mixture of water and propane, from  $T=278.15 \text{ K}$  to  $T=318.15 \text{ K}$  in steps of 5 K. The mass density data we used for liquid water were those recommended by Kell [108], and the vapor pressure of water was calculated using the Chebyshev polynomial representation of Ambrose and Lawrenson [109]. For the temperature range considered, these data are in good agreement with IAPWS-based recommendations [110, 111].

Somewhat surprisingly, experimental data on the partial molar volume at infinite dilution of propane dissolved in liquid water are rather scarce, and there is considerable scatter: only four papers in the literature report directly determined values for  $V_2^{L,\infty}$ . Masterton presented three results at 16.9 °C, 23.0 °C and 29.1 °C [112], Krichevsky and Ilinskaya gave one value at 25 °C [113], as did Moore et al. [114]. Zhou and Battino [115] report results at 25 °C and 30 °C: the 25 °C-values of the latter two papers appear to be too high. Thus, for expressing the temperature dependence of the partial molar volume at infinite dilution of propane in water we considered only Refs. [112, 113]:

**Table 3** Experimental “uncorrected” Henry fugacities (Henry’s law constants)  $\tilde{h}_{2,1}(T, P)$  at the indicated experimental temperatures  $T$  and total pressures  $P$ , product  $Z^V(T, P, y_2)\phi_2^V(T, P, y_2)$  and Poynting correction term  $C_2(T, P)$  of Eq. 6, Henry fugacity (Henry’s law constant)  $h_{2,1}(T, P_{\sigma,1})$  at the indicated temperature  $T$  and vapor pressure  $P_{\sigma,1}(T)$ , deviations  $\Delta_i = h_{2,1}^{\text{expt}}(T_i) - h_{2,1}^{\text{calc}}(T_i)$  between experimental values at temperature  $T_i$  and values calculated via Eq. 12, and Ostwald coefficients  $L_{2,1}^\infty(T, P_{\sigma,1})$  at infinite dilution.

$\frac{T}{\text{K}}$	$\frac{P}{\text{kPa}}$	$\frac{10^{-6}\tilde{h}_{2,1}(T,P)}{\text{kPa}}$	$Z^V\phi_2^V$	$C_2$	$\frac{10^{-6}h_{2,1}(T,P_{\sigma,1})}{\text{kPa}}$	$\frac{10^{-6}\Delta_i}{\text{kPa}}$	$10^2L_{2,1}^\infty(T, P_{\sigma,1})$
278.175	76.458	1.75899	0.97090	1.00197	1.7045	0.0042	7.5309
283.087	83.582	2.18851	0.97006	1.00216	2.1184	−0.0019	6.1645
288.141	77.088	2.67058	0.97390	1.00200	2.5957	−0.0091	5.1174
288.158	89.143	2.68236	0.96981	1.00231	2.5954	−0.0116	5.1183
293.132	88.647	3.22415	0.97166	1.00230	3.1256	−0.0051	4.3193
298.134	52.667	3.77272	0.98435	1.00133	3.7087	0.0149	3.6976
298.159	85.428	3.81612	0.97436	1.00221	3.7101	0.0134	3.6966
298.160	91.329	3.81990	0.97257	1.00237	3.7063	0.0094	3.7004
298.164	92.004	3.81651	0.97237	1.00239	3.7022	0.0049	3.7045
298.168	57.060	3.77368	0.98301	1.00145	3.7042	0.0064	3.7026
303.155	93.800	4.42902	0.97346	1.00242	4.3011	0.0153	3.2372
308.137	96.817	5.01940	0.97426	1.00249	4.8781	−0.0084	2.8961
313.132	100.082	5.65079	0.97479	1.00254	5.4943	0.0058	2.6077
318.127	98.616	6.22465	0.97686	1.00246	6.0657	−0.0105	2.3945
318.151	98.220	6.22987	0.97697	1.00239	6.0719	−0.0071	2.3922

For the significance of  $\tilde{h}_{2,1}(T, P)$  see Rettich et al. [46] and Refs. [39, 41, 43, 98]. Note that the tabulated temperatures refer to IPTS-68

$$\ln \left[ V_2^{L,\infty} / (\text{cm}^3 \cdot \text{mol}^{-1}) \right] = 4.0768 + 0.0048361t \quad (11)$$

where  $t = T/\text{K} - 273.15$ .

### 3 Results and Discussion

Our experimental results for the solubility of propane in liquid water are given in Table 3. As pointed out above, the work of Rettich et al. [39, 41, 43, 46, 98] should be consulted for the exact significance of the “uncorrected” Henry fugacity  $\tilde{h}_{2,1}(T, P)$  and the details of the data reduction formalism used. Please note that the Henry fugacity (Henry’s law constant)  $h_{2,1}(T, P_{\sigma,1}(T))$  refers to the vapor pressure of pure water at each temperature.

Once experimental Henry fugacities for a selected solvent/solute system have been collected over a desired temperature range, the question arises as to their most satisfactory mathematical representation as a function of temperature. In the absence of generally applicable theoretical models, one has to rely on essentially empirical fitting equations. Depending on the choice of variables, that is,  $T$  or  $1/T$ , for expanding the partial molar enthalpy change on solution (see below), either a Clarke-Glew type fitting

equation [81] or a Benson-Krause type fitting-equation [40, 42] is obtained. Based on its ability to fit our data we selected a three-term CG equation,

$$\ln \left( \frac{h_{2,1}}{\text{kPa}} \right) = 313.55051 - \frac{15651.9}{T/\text{K}} - 43.1640 \ln \left( \frac{T}{\text{K}} \right) \quad (12)$$

It performs somewhat better than the three-term BK equation.

$$\ln \left( \frac{h_{2,1}}{\text{kPa}} \right) = 2.987045 + \frac{10005}{T/\text{K}} - \frac{1904.2 \times 10^3}{(T/\text{K})^2} \quad (13)$$

A suitable measure of the dispersion of experimental results is the average percentage deviation.

$$\langle \delta \rangle = N^{-1} \sum_{i=1}^N |\delta_i| \quad (14)$$

where  $N$  denotes the number of individual data, whose percentage deviations  $\delta_i$  are calculated via

$$\left. \begin{aligned} \delta_i &= 100 \times \Delta_i / h_{2,1}^{\text{calc}}(T_i), \\ \Delta_i &= h_{2,1}^{\text{expt}}(T_i) - h_{2,1}^{\text{calc}}(T_i). \end{aligned} \right\} \quad (15)$$

Column 7 in Table 3 gives the deviations  $\Delta_i$  between the individual experimental values and values calculated with Eq. 12. The average percentage deviation for our measurements is  $\langle \delta \rangle = 0.25\%$  for the CG fit, while for the BK fit we have  $\langle \delta \rangle = 0.31\%$  (in doing the least squares fittings, average values were used at those temperatures for which multiple measurements exist: thus, fitting was done for nine points/temperatures).

Another useful measure of gas solubility is the Ostwald coefficient  $L_{2,1}(T, P)$ , a distribution coefficient that is preferably defined [3–5, 12, 46, 47, 97, 116, 117] as the ratio of the amount-of-substance densities (amount-of-substance concentrations) of solute 2 in the coexisting equilibrium phases liquid and vapor, respectively, at experimental temperature  $T$  and corresponding equilibrium pressure  $P$ :

$$L_{2,1}(T, P) = \left( \frac{\rho_{n,2}^{\text{L}}}{\rho_{n,2}^{\text{V}}} \right)_{\text{equil}} \quad (16)$$

Here,  $\rho_{n,2}^{\pi} = n_2^{\pi} / (n^{\pi} V^{\pi}) = x_2^{\pi} / V^{\pi} = x_2^{\pi} \rho_n^{\pi}$ ,  $n^{\pi} = n_1^{\pi} + n_2^{\pi}$ , where  $n_i^{\pi}$  is the amount of substance of component  $i$  of a mixture/solution phase  $\pi$  (either L or V) with total amount  $n^{\pi}$ ,  $V^{\pi}$  is the molar volume associated with phase  $\pi$ , and  $\rho_n^{\pi} = \sum_i \rho_{n,i}^{\pi} = 1 / V^{\pi}$  is the total amount-of-substance density of the solution in phase  $\pi$ . The history of the Ostwald coefficient has been discussed by Battino [117]; see also Ref [118]. Note that  $\rho_n^{\pi} = 1 / V^{\pi} = \rho_N^{\pi} / N_A$ , where  $\rho_N^{\pi} = N_A / V^{\pi}$  is the number density. For the exact relation between the Henry fugacity and the Ostwald coefficient see Wilhelm [3–5, 97, 116, 119, 120]. In the limit as  $\rho_{n,2}^{\text{V}} \rightarrow 0$ , and thus  $P \rightarrow P_{\sigma,1}$ , the *infinite dilution limit* of the Ostwald coefficient.



$$L_{2,1}^{\infty} = L_{2,1}^{\infty}(T, P_{\sigma,1}) = \lim_{\substack{\rho_{n,2}^V \rightarrow 0 \\ P \rightarrow P_{\sigma,1}}} L_{2,1}(T, P) = \lim_{\substack{\rho_{n,2}^V \rightarrow 0 \\ P \rightarrow P_{\sigma,1}}} \left( \frac{\rho_{n,2}^L}{\rho_{n,2}^V} \right)_{equil}, \text{ constant } T \quad (17)$$

is rigorously given by

$$L_{2,1}^{\infty}(T, P_{\sigma,1}) = \frac{RT}{h_{2,1}(T, P_{\sigma,1})V_1^{L,*}(T, P_{\sigma,1})} Z_1^{V,*}(T, P_{\sigma,1}) \phi_2^{V,\infty}(T, P_{\sigma,1}) \quad (18)$$

Here,  $Z_1^{V,*}(T, P_{\sigma,1}) = P_{\sigma,1}V_1^{V,*}(T, P_{\sigma,1})/RT$  is the compression factor of pure (\*) saturated water vapor,  $\phi_2^{V,\infty}(T, P_{\sigma,1})$  is the fugacity coefficient of propane at infinite dilution in water vapor at pressure  $P_{\sigma,1} = P_{\sigma,1}(T)$ , and  $V_1^{L,*}(T, P_{\sigma,1}) \equiv V_{\sigma,1}^{L,*}$  is the molar volume of pure liquid water at saturation (subscript  $\sigma$ ). Since most gas-solubility measurements are performed in the low to moderate pressure domain, use of the computationally convenient two-term volume-explicit virial equation yields.

$$Z_1^{V,*}(T, P_{\sigma,1}) \phi_2^{V,\infty}(T, P_{\sigma,1}) = \left( 1 + \frac{B_{11}}{RT} P_{\sigma,1} \right) \exp \left[ \frac{2B_{12} - B_{11}}{RT} P_{\sigma,1} \right] \quad (19)$$

The Ostwald coefficients  $L_{2,1}^{\infty}(T, P_{\sigma,1})$  at infinite dilution were calculated point-by-point from the experimental Henry fugacities  $h_{2,1}(T, P_{\sigma,1})$  according to Eqs. 18 and 19; they are included in Table 3. For the entire temperature range  $278.15 \leq T/\text{K} \leq 318.15$  they were fitted by a four-term BK equation.

$$\ln \left( L_{2,1}^{\infty}(T, P_{\sigma,1}) \right) = 51.614299 - \frac{47.653173 \times 10^3}{T/\text{K}} + \frac{13.016534 \times 10^6}{(T/\text{K})^2} - \frac{1.100098 \times 10^9}{(T/\text{K})^3} \quad (20)$$

In doing the least squares fitting, average values were again used at those temperatures for which multiple measurements exist, that is, fitting was done for nine points/temperatures.

For convenience, Table 4 presents smoothed values of the Henry fugacity (Henry's law constant)  $h_{2,1}(T, P_{\sigma,1})$  at 5 K intervals from  $T=278.15$  K to 318.15 K., calculated from Eq. 12. Partial molar enthalpy changes on solution  $\Delta H_2^{\infty}(T, P_{\sigma,1})$ , and partial molar heat capacity changes on solution  $\Delta C_{p,2}^{\infty}(T, P_{\sigma,1})$  were also calculated from Eq. 12 (van 't Hoff analysis) using the customary relations.

$$\Delta H_2^{\infty}(T, P_{\sigma,1}) = -RT^2 \frac{d \ln h_{2,1}}{dT} \quad (21)$$

and

$$\Delta C_{p,2}^{\infty}(T, P_{\sigma,1}) = \frac{d\Delta H_2^{\infty}}{dT} \quad (22)$$

For the temperature range considered in this work, the contributions of the additional terms appearing in the more rigorous expressions [3–5, 97, 119–121] are very small and well within the experimental uncertainty band. Of note is the quite reasonable agreement with the van 't Hoff results obtained from a critical evaluation of older measurements as published in the review article by Wilhelm et al. [2] more than 40 years ago. To facilitate comparison, these values are shown in *italics*.

**Table 4** Henry fugacities (Henry's law constants)  $h_{2,1}(T, P_{\sigma,1})$  and Ostwald coefficients  $L_{2,1}^{\infty}(T, P_{\sigma,1})$  at infinite dilution for propane dissolved in liquid water at selected temperatures  $T$  and corresponding vapor pressures  $P_{\sigma,1}(T)$  of pure liquid water [109].

$T/\text{K}$	$\frac{10^{-6}h_{2,1}(T, P_{\sigma,1})}{\text{kPa}}$	$L_{2,1}^{\infty}(T, P_{\sigma,1})$	$\frac{\Delta H_2^{\infty}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{cal}}H^{\infty}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta C_{p,2}^{\infty}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$	$\frac{\Delta_{\text{cal}}C_p^{\infty}}{\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}$
278.15	1.6983	0.07541	−30.31 −29.9 <sup>f</sup>	−29.66 <sup>c</sup>	359	335.7 <sup>c</sup>
283.15	2.1261	0.06152	28.52 −28.0 <sup>f</sup>	−27.99 <sup>c</sup>	359	331.6 <sup>c</sup>
288.15	2.6063	0.05108	−26.72 −26.2 <sup>f</sup>	−25.84 <sup>b</sup> , −26.34 <sup>c</sup>	359	327.4 <sup>c</sup>
293.15	3.1325	0.04315	−24.93 −24.3 <sup>f</sup>	−24.72 <sup>c</sup>	359	323.2 <sup>c</sup>
298.15	3.6958	0.03710	−23.14 −22.5 <sup>f</sup>	−23.27 <sup>a</sup> , −23.11 <sup>c</sup>	359	332 <sup>b</sup> , 319.0 <sup>c</sup> , 389 <sup>d</sup>
303.15	4.2853	0.03244	−21.34 −20.6 <sup>f</sup>	−21.53 <sup>c</sup>	359	314.9 <sup>c</sup>
308.15	4.8883	0.02885	−19.55 −18.8 <sup>f</sup>	−19.19 <sup>b</sup> , −19.96 <sup>c</sup>	359	310.7 <sup>c</sup>
313.15	5.4909	0.02607	−17.75 −17.0 <sup>f</sup>	−18.42 <sup>c</sup>	359	306.5 <sup>c</sup>
318.15	6.0791	0.02395	−15.96 −15.1 <sup>f</sup>	−16.90 <sup>c</sup>	359	302.4 <sup>c</sup>

Partial molar enthalpy changes on solution  $\Delta H_2^{\infty}$  and partial molar heat capacity changes on solution  $\Delta C_{p,2}^{\infty}$  obtained via van 't Hoff analysis (see Eqs. 21 and 22) are compared with molar enthalpies of solution  $\Delta_{\text{cal}}H^{\infty}$  and molar heat capacity changes on solution  $\Delta_{\text{cal}}C_p^{\infty}$  (at low partial pressures of gas) obtained via high-precision calorimetry [122–126]. For full information, the van 't Hoff results for  $\Delta H_2^{\infty}$  reported in Ref. [2] are shown in *italics*; note that the three-term CG equation used in Ref. [2] to fit the solubility data yields a constant value  $\Delta C_{p,2}^{\infty} = 368 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

<sup>a</sup>Ref. [122]. <sup>b</sup>Ref. [123]. <sup>c</sup>Ref. [124]. <sup>d</sup>Ref. [125]. <sup>e</sup>Ref. [126]. <sup>f</sup>Ref. [2]

A stringent test of the quality of the experimental data is to compare the derived enthalpy changes (one differentiation level) and heat capacity changes (two differentiation levels) with *directly* obtained high-precision calorimetric results [5, 88, 89]. Table 4 also lists results for molar enthalpies of solution  $\Delta_{\text{cal}}H^{\infty}$  obtained via *calorimetry* at low partial pressure of gas (usually less than 100 kPa): Dec and Gill [122, 123] at 298.15 K, and at 288.15 K, 298.15 K, and 308.15 K, respectively, Naghibi et al. [124] from 273.15 K to 323.15 K (Boulder group, Colorado, USA), Olofsson et al. [125] at 288.15 K, 298.15 K, and 308.15 K, and Hallén and Wadsö [126] at 298.15 K (Lund group, Sweden). The accord is entirely satisfactory. This strongly supports that our results are essentially free from systematic errors.

The *three-term* CG equation Eq. 12, provides the most reasonable fit for our data. Note, however, that this choice results in a temperature *independent* value  $\Delta C_{p,2}^{\infty} = 359 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  that has thus to be considered as an *average* value for the mid-point of the temperature range covered: hence the agreement with the calorimetrically derived heat capacity changes is quite reasonable. We do not consider our data to be sufficiently precise to use a four-term CG fit that would yield temperature-dependent

$\Delta C_{P,2}^{\infty}$  values. Compared to our gas solubility measurements on the systems methane dissolved in water or ethane dissolved in water [46] a somewhat greater experimental uncertainty (reasons unknown) has been encountered in measuring solubilities for the present system. Nevertheless, we believe that our new values for the Henry fugacity  $h_{2,1}(T, P_{\sigma,1})$  and the Ostwald coefficient  $L_{2,1}^{\infty}(T, P_{\sigma,1})$  at infinite dilution of propane dissolved in pure liquid water are the most reliable ones to date.

Financial support for this work from the National Institutes of Health is acknowledged. We also thank Professor D. A. Dolson for performing some of the calculations.

**Author contributions** Experimental aspects: T. R. Rettich, R. Battino, and E. Wilhelm. E. Wilhelm wrote the main manuscript text. All authors reviewed the manuscript.

**Funding** Open access funding provided by University of Vienna. This research was supported by National Institutes of General Medical Sciences, GM (14710-13).

## Declarations

**Competing interests** The authors declare no competing interests.

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