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Thermodynamics of Non-Reactive Gases Dissolved in Water at Ambient Temperature ($T \leq 333$ K): an Update

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Abstract The thermodynamics of dissolution of non-reactive gases in water under ambient conditions is of importance for the description of the properties of small hydrophobic solutes, and they are also of interest for environmental assessments. The review published in 1977 by Wilhelm, Battino and Wilcock (Chem. Rev. 77:219–262, 1977) constitutes a milestone in this field. However, a number of new data have been published since then, including both solubility and calorimetric determinations. We have analyzed the new data for 27 binary systems reported in the literature at the time of writing this article. Whenever solubility and calorimetric data both exist they have been fitted together. There are, however, systems for which only one type of new thermodynamic information is available; these systems were also analyzed using procedures that are described in this work.

Keywords Gaseous solutes · Aqueous solutions · Gibbs energy and enthalpy of dissolution · Ambient temperatures

1 Introduction

The thermodynamics of non-reactive gases dissolved in water under ambient conditions is of great interest for physical chemistry as well as for environmental chemistry. The knowledge of the thermodynamics of the dissolution of gases in water has been based to a large extent on the fundamental and thorough work published in 1977 by Wilhelm et al. [1]; this work has been the obligatory reference in the field. Since that review was published thirty one years ago, important new solubility data for gases dissolved in water, many of which had been already studied, have become available. Moreover, in many cases the precision of the

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newer data was greatly improved over the earlier. Also, since [1] was published, several studies became available that reported calorimetric data for gases dissolved in water.

The goal of the present work is to provide an update of equations that are able to describe the Gibbs energy (ΔG_2^∞) and enthalpy (ΔH_2^∞) of dissolution of gaseous solutes as a function of temperature within the ambient-temperature region. For those systems where calorimetric as well as new solubility data are available, the updated equations we report in the present work were obtained by fitting together both sets of data. Hence, they can describe both types of thermodynamic quantities, Gibbs energy and enthalpy of dissolution. We have also analyzed systems for which either solubility or calorimetric data have become available since 1977.

We have limited the range of temperature considered in this work to ambient conditions due to the fact that there are in general two experimental techniques to determine solubility of gases in liquids. One applies over the complete range of temperatures (i.e., triple point solvent to its critical point), which we refer to as the high-temperature technique. In the other, denoted as the low-temperature technique, the solvent's vapor pressure is in general lower than, or sometimes slightly above, 0.1 MPa. There is a big difference in the experimental uncertainties of each technique as we have discussed in previous articles [2, 3]; this suggests that it is inconvenient to mix the data at ambient temperatures with those at high temperatures, in order to maintain the higher precision of the first type of data. On the other hand, calorimetric data are very scarce for gases in water at higher temperature, and there again the uncertainty is much greater. An exception is H_2S because the data we used were determined with the high-temperature technique but the authors determined solubilities over a wide pressure range. The value of 333 K as the upper limit temperature of our study is certainly arbitrary, but the main number of sources using the low-temperature technique are covered by this limit in temperature.

2 General

2.1 Strategy Employed to Obtain an Equation for $\Delta G_2^\infty(T)$ (i.e., $\ln k_H$)

The literature was surveyed to identify gas solubility data in water that were published after the important and comprehensive review of Wilhelm et al. [1], as well as calorimetric data for the same type of solutions. For those systems that have been already analyzed in [1], only new solubility data having higher precision together with calorimetric data, whenever available, were used in the present work to fit the parameters of expressions for $\Delta G_2^\infty(T)$. It is useful to divide the systems analyzed here into five different types according to the type and precision of the new information that is available:

A) Benchmark systems (solutes O_2, Ar, CH_4). There are very precise new information of the solubility of these solutes, hence of Henry's constant k_H, and also there are independent calorimetric data. For these systems a very detailed analysis was performed which was then used to establish the best procedure for all the other gas + water binary systems considered here. For this group of systems the fitting procedure included a simultaneous fit of the solubility and calorimetric data.
B) Inert gases (besides Ar). They were analyzed similarly to group A, but there is only one new source of precise solubility data, hence of $\Delta G_2^\infty(T)$.
C) Systems for which the new information available was less abundant and/or precise than systems of type A. The procedure employed was the same as for the two previous type systems.

D) Systems for which new solubility data of good precision are available, but there are no calorimetric data.
E) Some small hydrocarbons and other solutes for which there are no new solubility data, but calorimetric data have been published. For some systems of this type we used ΔG_2^∞ from [1] (as detailed below) to fit them together with the calorimetric data using a single fitting procedure. We also include in this type some systems for which only new solubility data of intermediate precision are available. The details about each subtype are described below.

Because the pressure(s) at which solubilities have been determined in the various sources that we have used are close to atmospheric pressure, the Poynting correction in general was not relevant to the formulation of ΔG_2^∞ close to the water-saturation line. The exceptions are for data of very high precision; in those cases, however, the authors have already corrected the data to the vapor pressure of water. Some data in the ambient temperature range that were obtained using the high-temperature technique [2, 3] have not been considered by us, due to the already mentioned lower precision of the high-temperature technique.

2.2 Fitting Equations

For all of the systems we adopted a Valentiner-type polynomial for $\ln k_\mathrm{H}$

$$\ln(k_\mathrm{H}/\mathrm{bar}) = a_0 + \frac{a_1}{T/\mathrm{K}} + a_2 \ln(T/\mathrm{K}) + \sum_{i=1}^{n} a_{i+2}(T/\mathrm{K})^i \tag{1}$$

which has an acceptable temperature dependence because it includes the term a_2 which represents the contribution of a temperature independent term for $\Delta C_{p,2}^\infty$. Many of the very precise recent data for $\ln k_\mathrm{H}$ make use of a polynomial in powers of the reciprocal temperature. However this implies that $\Delta C_{p,2}^\infty$ is not independent of temperature. Assuming a constant heat capacity over such a restricted temperature range, i.e., $T \leq 333$ K, seems a more realistic assumption than using a temperature dependent heat capacity; the effect of this simplifying assumption will be discussed below.

In the present work the standard state for the dissolved solute is the ideal solution (according to Henry's law) at a solute mole fraction of unity; for the gaseous solute the standard state is the ideal gas at 0.1 MPa. Under these conditions the relation between Henry's constant and $\Delta G_2^\infty(T)$ is,

$$\Delta G_2^\infty(T) = RT \ln\left\{\frac{k_\mathrm{H}}{p^\theta}\right\} \tag{2}$$

where p^θ is the standard pressure of 0.1 MPa. Assuming a constant value for $\Delta C_{p,2}^\infty$, we have for the Gibbs energy of dissolution the following equation,

$$\Delta G_2^\infty(p^\theta, T) = (\Delta H_0 - \Delta C_{p2}^\infty T_0) + \left(\frac{\Delta G_0 - \Delta H_0}{T_0} + \Delta C_{p2}^\infty\right) T - \Delta C_{p2}^\infty T \ln\left(\frac{T}{T_0}\right) \tag{3}$$

where the subscript $_0$ denotes the value of the quantity at $T_0 = 298.2$ K. It may be seen that Eq. 3 contains the contributions of the calorimetric data as well as those of the gas solubility. The use of a constant $\Delta C_{p,2}^\infty$ is not only justified by the restricted ambient temperature range covered in this study, but also practically because there are no calorimetric information on the dependence of $\Delta C_{p,2}^\infty$ with temperature for aqueous solutions of gaseous substances. Below we give numerical results that further support our contention. An important part of the

analysis in the present work will be based upon the values of k_H because their uncertainties are directly related to the experimental uncertainty of the solubility data. Thus, the relative precision of k_H is related to the uncertainty in $(\Delta G_2^\infty/RT)$ by,

$$\delta\left(\frac{\Delta G_2^\infty(T)}{RT}\right) = \delta\left(\ln\frac{k_H(T)}{p^\Theta}\right) = \frac{\delta k_H}{k_H} \tag{4}$$

As mentioned above, the Poynting correction was negligible because at ambient temperature and low gas pressure this correction is usually below experimental uncertainty. Nevertheless, if it were necessary, the Poynting correction for ambient temperatures, including the solubility of a gas at higher solute partial pressures, can be easily determined using experimental values of V_2^∞ as a pressure independent quantity. In this way, instead of Eq. 3 the complete equation for $\Delta G_2^\infty(p,T)$ becomes:

$$\Delta G_2^\infty(p,T) = \Delta G_2^\infty(p^\Theta,T) + V_2^\infty(T)(p-p^\Theta) = RT\ln\left(\frac{k_H}{p^\Theta}\right) \tag{5}$$

Reference [4] reviewed some of the data available in 1988 and reported smoothed values, but we have used it only as a guide to the sources they analyzed. On the other hand, [5] reported solubility data obtained using a chromatographic technique that has lower precision, so again they are only employed for SF_6 due to the lack of other information, and for some other systems only for the purpose of comparison.

3 Analysis of Data for the Three Benchmark Systems

3.1 Oxygen

Very precise new determinations of the solubility of O_2 in water have been reported [6, 7] covering the temperature range 273 to 333 K. Both sources determined the solubilities of O_2 by employing very precise techniques (relative uncertainties of order 0.01%), and corrected them for non-ideality in the vapor phase and the Poynting effect. Rettich et al. [6] give solubilities in the temperature range 275 to 328 K). Benson et al. [7] reported data over the range (273 to 333 K) and they calculated the final values of k_H using an extrapolation procedure to $p \to 0$; this procedure should account also for the eventual effect of solute non-ideality in the solution phase. The relative differences in k_H between both sources (δ%) are given in Table 1. Both sets of data were refitted using Valentiner equations, Eq. 3. The two sets of data were found to be consistent with differences smaller than 0.4%.

As a preliminary test we compare in Table 2 the experimental k_H values reported in [6, 7] with those calculated at several temperatures using Eq. 3. For this calculation we used calorimetric data from [8]: $\Delta C_{p,2}^\infty = 205$ J·mol^{-1}·K^{-1} and $\Delta H_2^\infty(298.15\text{ K}) = -12.00$ kJ·mol^{-1}; $\Delta G_2^\infty(298.15\text{ K})$ was an average of experimental values as explained below. Table 2 shows

Table 1 Differences between k_H values for the $O_2 + H_2O$ system from two sources [6, 7]

T/K	δ(%)[a]
273.15	−0.015
298.15	0.002
328.15	−0.39

[a]Percent difference of value from [6] minus value from [7] divided by value from [6]

Table 2 Comparison of experimental data with calculated values for the $O_2 + H_2O$ system

T/K	$10^{-4} \times k_H$/bar		
	Experimental value and reference number		Calc.
273.15	2.5598 [6]	2.5602 [7]	2.5655
283.15	3.2959 [6]	3.2950 [7]	3.2960
298.15	4.4039 [6]	4.4038 [7]	4.4039
313.15	5.3990 [6]	5.4063 [7]	5.3937
328.15	6.1900 [6]	6.2139 [7]	6.1432

Table 3 Calorimetric data for the $O_2 + H_2O$ system

T/K	ΔH_2^∞/ kJ·mol^{-1}			$\Delta C_{p,2}^\infty$/ J·K^{-1}·mol^{-1}
	Experimental value and reference number			
288.15		−14.03±0.06 [8]		
298.15	−12.06±0.04 [9]	−12.00±0.05 [8]	−12.031±0.036 [10]	205±2 [8]
308.15		−9.92±0.10 [8]		

that the results obtained from both experimental sources coincide very well with the calculated values up to 313 K. However, the agreement is less satisfactory at 328.15 K, but it should be noted that at this temperature the discrepancy between the two experimental sources of solubility is somewhat larger than at lower temperatures, as shown in Table 2.

There are three sources of calorimetric data for this system, [9] and [10] each give a single value of ΔH_2^∞ at 298.15 K. One study [8] published values of ΔH_2^∞ at three temperatures and from them the authors calculated $\Delta C_{p,2}^\infty$. The values of these calorimetric data are reported in Table 3.

3.2 Argon

For this solute we used the results from two new experimental studies of its solubility in water [11, 12]. Their values were corrected to the saturation pressure by the authors using the same procedure as for O_2. The resulting k_H data have a high precision, and their uncertainties are around 0.04 to 0.05%. According to [11], the correction for non-ideality was found to amount to 0.2%. Values of $10^{-4} \times k_H(298.2\ \text{K})$ from the two sources are 4.0020 bar [11] and 4.0041 bar [12]; hence the agreement between both experimental studies for $T = 298.2$ K is also remarkably good. In the case of [12] the value of the constant R was corrected to the value given in IUPAC's Green Book, $R = 8.3145$ J·mol^{-1}·K^{-1} [13].

We made a test for this system by calculating k_H at four temperatures with Eqs. 2 and 3, and using calorimetric data from [8]: $\Delta C_{p,2}^\infty = 200$ J·mol^{-1}·K^{-1} and $\Delta H_0 = \Delta H_2^\infty(T_0) = -12.01$ kJ·mol^{-1} and $\Delta G_2^\infty(T_0) = \Delta G_0 = 26.27$ kJ·mol^{-1} from the average of the experimental solubility values reported in [11, 12] at T_0. The values of the coefficients of Eq. 3 are −71.640 kJ·mol^{-1} and 328.393 kJ·mol^{-1} for the independent and linear terms, respectively. The results are given in Table 4 where we compare the k_H values calculated at the low- and high-temperature ranges with the experimental values reported in [11] and [12],

As was the case for the other benchmark systems, there is a tendency for the agreement between calculated and experimental values to worsen when temperature is higher. For Ar + H_2O this is more notable in [12] than in [11] because the temperature range in the latter study is smaller.

Table 4 Comparison of experimental data with calculated values for the Ar + H_2O system

T/K	$10^{-4} \times k_H$/bar		
	Experimental value and reference number		Calc.
273.15		2.3374 [12]	2.3362
283.15	3.0006 [11]	3.0033 [12]	2.9972
313.15	4.9102 [11]	4.9079 [12]	4.9062
333.15		5.8353 [12]	5.7724

3.3 Methane

The source of new solubility data was [14]. The calorimetric data were taken from [8, 15, 16]. One of these sources [15] reported a single value of ΔH_2^∞ at 298.2 K, whereas the other two sources reported measurements of enthalpies of dissolution at several temperatures: 288.15, 298.15 and 308.15 K in [8] and at eleven temperatures in the range (273 to 323) K in [16]. In these two cases the authors calculated a constant average $\Delta C_{p,2}^\infty$ value and the values of $\Delta C_{p,2}^\infty$ at all temperatures, respectively.

As shown in Table 5, the values of ΔH_2^∞(298.15 K) for the three sources agree within their experimental precision. However, there are differences in $\Delta C_{p,2}^\infty$ in the two sources where its value was calculated, as shown in Table 5.

We have used Eqs. 2 and 3 to calculate k_H for aqueous CH_4 solutions at the extreme temperatures of 273.15 and 333.15 K, with a value of $\Delta H_2^\infty(298.15\ \text{K}) = -13.12\ \text{kJ·mol}^{-1}$ that is the average value from the three sources. For this preliminary comparison we used for $\Delta C_{p,2}^\infty$ at 298.2 K the values reported in each source publication in order to estimate the effect of a different heat capacity, and compared them with the values of k_H obtained with a Valentiner polynomial fitted to the new experimental data. The results of this comparison are reported in Table 6.

Using the value of heat capacity reported in [8], the difference from the values calculated with Eqs. 2 and 3 is 0.4% at the lowest and 1.8% at the highest temperatures, respectively. The value of the heat capacity reported in [16] for 298.2 K gave larger differences, which at the extremes of the temperature range were 2.0% and 4.2%, respectively. The value reported by [8] gives a picture that is more consistent with the solubility data; nevertheless, the difference is larger than the experimental uncertainty of the solubility data.

It should be borne in mind that the comparisons in Tables 2, 4 and 6 are given in order to evaluate the consistency among the data from solubility and from calorimetry. The tables report values of k_H calculated using an average value of ΔG_2^∞(298.15 K) when two sources of solubility data exist (at this temperature they were very close, cf., Tables 2 and 4), and the reported calorimetric quantities.

4 Number of Coefficients in the Valentiner Equation

In order to assess the number of coefficients that are necessary in Eq. 1 to obtain a good adjustment of the data, we analyzed the performance of equations having between three and five coefficients. The characteristics of the data sets used for the benchmark gases are given in Table 8, and the results of this assessment are reported in Table 7, where the columns with the heading (σ_{coef}/coef.) give the ratio of the standard deviation of the coefficients divided by the value of the corresponding coefficient. It should be noted that all of the coefficients in each fitting equation had an almost identical value for this quantity, so for each system only

Table 5 Summary of calorimetric data for the $CH_4 + H_2O$ system

T/K	ΔH_2^∞/ kJ·mol^{-1}			$\Delta C_{p,2}^\infty$/ J·K^{-1}·mol^{-1}	
	Value and reference number			Value and reference number	
288.15	−15.53±0.09 [8]		−15.24±0.06 [16]		−216.1±4 [16]
298.15	−13.06±0.15 [8]	−13.18±0.07 [15]	−13.12±0.07 [16]	−242±6 [8]	−209.0±2.9 [16]
308.15	−10.70±0.09 [8]		−11.06±0.07 [16]		−201.8±5.8 [16]

Table 6 Comparison of experimental data with calculated values for the $CH_4 + H_2O$ system

T/K	$10^{-4} \times k_H$/bar		
	Expt.	Value calculated with heat capacities in the given reference number	
273.15	2.1708	2.1794 [8]	2.2143 [16]
333.15	5.7196	5.8217 [8]	5.9643 [16]

Table 7 Effect of the number of fitting coefficients on the standard deviation of the fits and of each coefficient

	5 coefficients		4 coefficients		3 coefficients	
	Overall σ	σ_{coef}/ coef.	Overall σ	σ_{coef}/ coef.	Overall σ	σ_{coef}/ coef.
O_2	0.0036	0.3	0.0038	0.1	0.0046	0.004
Ar	0.0019	0.3	0.0019	0.05	0.003	0.003
CH_4	0.007	0.2	0.0086	0.2	0.009	0.01

a single value for the standard deviations of the coefficients is reported in Table 7. It was clear that increasing the number of coefficients of the fitting equation did not significantly improve the overall standard deviation (σ) but it decreased very much the reliability of the coefficient values.

In Fig. 1 we plot $\Delta \ln k_H$ against temperature for Ar dissolved in water. The ordinate is the difference in $\ln k_H$ between our fitted three-coefficient Valentiner equation (which was obtained including the calorimetric data) and other expressions for $\ln k_H$. One of the curves shows the difference between our three-coefficient Eq. 3 with the equation given in the 1977 review for the same system [1]. It may be noted that there is an appreciable difference between the new data and those that were the basis for previous formulations [1] for the solubility of Ar in water, the difference being a few percent.

With reference to the difference between our fitted equation (solubility as well as calorimetric data) and the new solubility data for this system [11, 12], Fig. 1 shows that there is a very good agreement, between 0.1 and 0.2%, but which becomes somewhat less satisfactory at the highest temperature where the difference reaches almost 0.5%.

It was also important to compare the performance of Valentiner type fitting equations having different numbers of coefficients. We plotted in Fig. 1 the results of fitting the calorimetric and new solubility data with a four-coefficient fitting equation. It can be seen that the performance of the fitting equations was not altered in essence by adding one more coefficient, as shown in Fig. 1. The differences between the k_H values are at most 0.2% at the highest temperature, but the discrepancy is usually smaller than 0.1%. The same type of behavior was observed for the $O_2 + H_2O$ system when increasing the number of coef-

Table 8 Sources of data that were fitted to Eq. 6

	ΔG_2^∞			ΔH_2^∞		
	References	Number of points	T range	References	Number of points	T range
O_2	[6, 7]	69	273–333	[8–10]	72	288–308(3)
Ar	[11, 12]	69	275–328	[8, 17]	17	288–308(3)
CH_4	[14]	16	275–328	[8, 15, 16]	32	273–323(3)
He	[12]	32	274–333	[8, 17, 18]	30	288–308(3)
Ne	[12]	34	273–333	[8, 17]	22	288–308(3)
Kr	[12]	36	273–333	[8, 17]	10	288–308(3)
Xe	[12]	30	273–333	[8, 17]	14	288–308(3)
C_2H_6	[14]	23	275–323	[15, 19]	31	273–323(11)
$CClF_3$	[20]	4	288–318	[21]	5	287–318(5)
CCl_2F_2	[20]	4	288–318	[21]	5	278–313(5)
CF_4	[20, 22, 23]	10	278–318	[18, 21]	5	288–308(3)
SF_6	[5, 22]	9	278–298	[18]	3	288–308(3)
N_2	[26]	17	278–323		–	–
CO	[25]	14	278–323		–	–
C_3H_8	[1]	25	273–347	[8, 15, 18, 19]	36	273–323(11)
i-C_4H_{10}	[1]	14	278–343	[8, 27]	14	273–308(8)
n-C_4H_{10}	[1]	36	273–349	[14, 26]	35	273–318(10)
C_3H_6	[1]	7	294–361	–	–	–
c-C_3H_6	[1]	14	298–361	–	–	–
C_2F_6	[22, 23, 28]	16	278–328	–	–	–
c-C_4F_8	[20]	4	288–318	–	–	–
H_2S	[29]	7	273–333	–	–	–

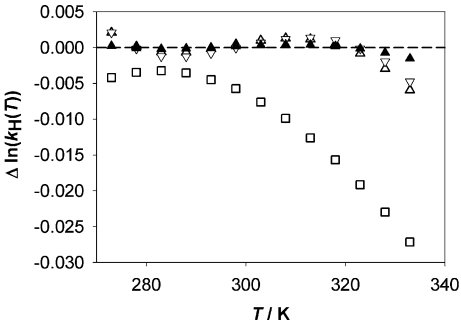

Fig. 1 Difference of $\ln k_H$ for Ar in water between our three-coefficient fitted equation and other equations. ▲, present work with four-coefficient equation; □ [1], △ [11], ▽ [12]

ficients of the fitting equation. We concluded that the relatively small discrepancy between experimental and fitted data cannot be resolved by the use of a fitting equation having more adjustable coefficients. Moreover, increasing the number of adjustable coefficients decreases their reliability (cf. Table 7).

This analysis of comparative performances shows that for type A systems a Valentiner polynomial having three coefficients is the best choice. This implies that a constant $\Delta C_{p,2}^\infty$, is able to give a very good fit by adjusting the value of the heat capacity to an average over

Table 9 Coefficients of Eq. 6 and their standard errors

Type	Gaseous solute (σ_{ov})[a]			Type	Gaseous solute (σ_{ov})[a]		
	a/ kJ·(mol·K)$^{-1}$	b/ kJ·(mol·K)$^{-1}$	c/ kJ·(mol·K)$^{-1}$		a/ kJ·(mol·K)$^{-1}$	b/ kJ·(mol·K)$^{-1}$	c/ kJ·(mol·K)$^{-1}$
A	O_2(0.0046)			C	SF_6(0.030)		
	1.4287	−69.9638	−0.1940		3.0417	−148.130	−0.42864
	(0.0052)	(0. 2319)	(0.0077)		(0.250)	(10.98)	(0.0374)
	Ar (0.003)				CF_4(0.077)		
	1.4249	−69.7486	−0.19357		2.66713	126.289	−0.37555
	(0.00566)	(0.2522)	(0.00084)		(0.35)	(15.469)	(0.053)
	CH_4(0.009)			D	N_2(0.0026)		
	1.6449	−80.5494	−0.22583		1.5452	−73.5664	−0.21131
	(0.0180)	(0.8050)	(0.00268)		(0.0124)	(0.5545)	(0.0018)
B	He (0.0073)				CO (0.0021)		
	0.92258	−37.2224	−0.12269		1.5488	−74.1139	−0.21222
	(0.0121)	(0.53712)	(0.00180)		(0.0069)	(0.5977)	(0.0020)
	Ne (0.0035)			Eb	C_3H_8(0.400)		
	1.04386	−45.3072	−0.13943		2.3485	−120.401	−0.3260
	(0.0069)	(0.3105)	(0.00103)		(0.0399)	(1.771)	(0.00596)
	Kr (0.0046)				n-C_4H_{10}(0.168)		
	1.5675	−79.2284	−0.21383		2.7949	−142.3657	−0.3911
	(0.0087)	(0.3898)	(0.0013)		(0.0196)	(0.8549)	(0.854)
	Xe (0.0041)				i-C_4H_{10}(0.632)		
	1.8002	−92.9576	−0.24744		3.1910	−158.762	−0.4501
	(0.0078)	(0.3521)	(0.0012)		(0.0878)	(3.827)	(0.0131)
C	C_2H_6(0.0064)			Ec	C_2F_6 (0.134)		
	2.0823	−105.408	−0.28838		4.4257	−210.8971	−0.63259
	(0.0154)	(0.6855)	(0.0023)		(0.779)	(35.4187)	(0.1158)
	$CClF_3$(0.203)				c-C_4F_8(0.00075)[b]		
	2.7422	−135.7462	−0.38536		5.3095	−255.1679	−0.76279
	(0.5229)	(23.3259)	(0.078)		(0.0153)	(0.691)	(0.00228)
	CCl_2F_2(0.092)				H_2S (0.048)		
	2.6781	−137.564	−0.37472		0.73783	−44.7505	−0.093961
	(0.224)	(9.899)	(0.0034)		(0.212)	(9.8217)	(0.0314)

[a]Overall standard deviation

[b]This value is unrealistically low due to availability of only four data points

Values in parenthesis under the value of each coefficient give the standard deviation of the corresponding parameter

the corresponding temperature range. For example, according to the fitted equations (see coefficient c in Table 9) the values of $\Delta C^{\infty}_{p,2}$ obtained by fitting the data with the three-coefficient Valentiner equation for O_2 and Ar was 5% smaller than the value determined by calorimetry. For CH_4 the resulting value of $\Delta C^{\infty}_{p,2}$ is an average between the two different

calorimetric values reported in the literature. Consequently, this strategy was adopted for all the gaseous solutes studied in this work.

5 Thermodynamic Equations

The fitting procedure was carried out for all the systems using an expression based upon Eq. 3. In order to simplify the notation in the table of results, ΔG_2^∞ (in kJ·mol^{-1}) is given by the following three-coefficient Valentiner equation,

$$\Delta G_2^\infty = RT\ln(k_{\mathrm{H}}/10^5\ \mathrm{Pa}) = aT + b + cT\ln(T/\mathrm{K}) \tag{6}$$

Coefficients b and c are related to the enthalpy and heat capacity by:

$$\begin{aligned} \Delta H_2^\infty &= b - cT, \\ \Delta C_{p2}^\infty &= -c \end{aligned} \tag{7}$$

6 Results

The sources and characteristics of the data employed for each system are identified in Table 8. The fitting equations are valid for the temperature range of ΔG_2^∞ as reported in the fourth column of this table. Table 9 reports the values of the three coefficients of Eq. 6, obtained by fitting the data for all of the studied systems. Figures 2 to 5 show the performance of the fitted data for describing ΔG_2^∞ and ΔH_2^∞ for one representative gas of each type of system for which there are new solubility and calorimetric data. The systems of type A, B and C can be described very satisfactorily with the coefficients reported in Table 9. Figure 2 shows the data for CH_4 and that the performance of the fitted equation in describing the two types of data was very satisfactory for this system. The same is true for the noble gases as shown in Fig. 3 for the Kr + H_2O system, and also for C_2H_6 + H_2O as shown in Fig. 4. On the other hand, Fig. 5 illustrates the behavior of SF_6 dissolved in water; for this system it is obvious that the coefficients obtained by fitting solubility and calorimetric data together do not represent the two sets of data with similar success; this is discussed in the next section.

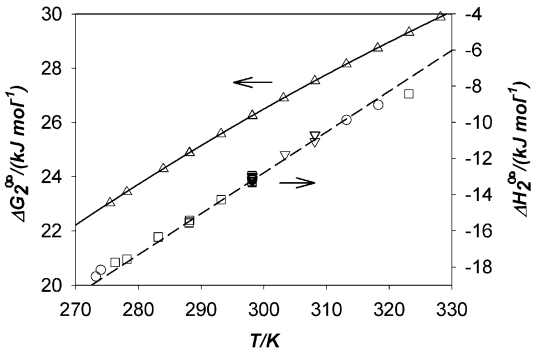

Fig. 2 Plot of ΔG_2^∞ and ΔH_2^∞ against temperature for CH_4 in water. ΔG_2^∞: *solid line*, three-coefficient Valentiner equation; and experimental points △ [14]. ΔH_2^∞: *dashed line*, three-coefficient Valentiner equation; and experimental points ○ [8], ▽ [15], □ [16]

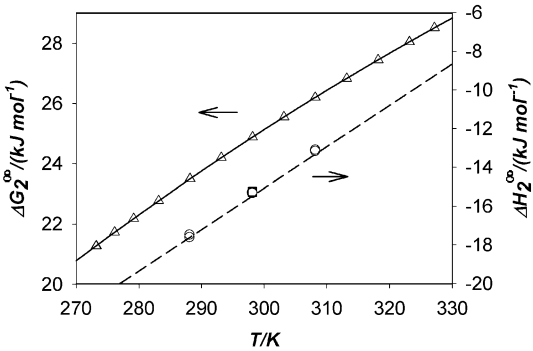

Fig. 3 Plot of ΔG_2^∞ and ΔH_2^∞ against temperature for Kr in water. ΔG_2^∞: *solid line*, three-coefficient Valentiner equation; and experimental points △ [12], ΔH_2^∞: *dashed line*, three-coefficient Valentiner equation; and experimental points ○ [8], □ [17]

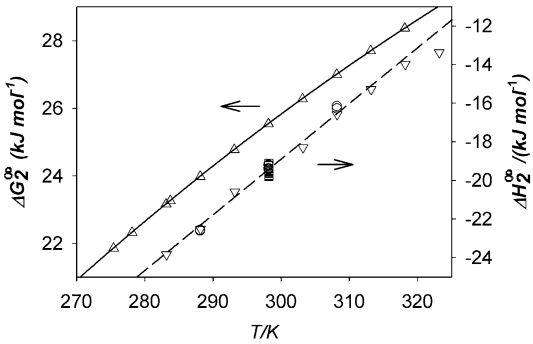

Fig. 4 Plot of ΔG_2^∞ and ΔH_2^∞ against temperature for C_2H_6 in water. ΔG_2^∞: *solid line*, three-coefficient Valentiner equation; and experimental points △ [14]. ΔH_2^∞: *dashed line*, three-coefficient Valentiner equation; and experimental points ○ [8], □ [15], ▽ [19]

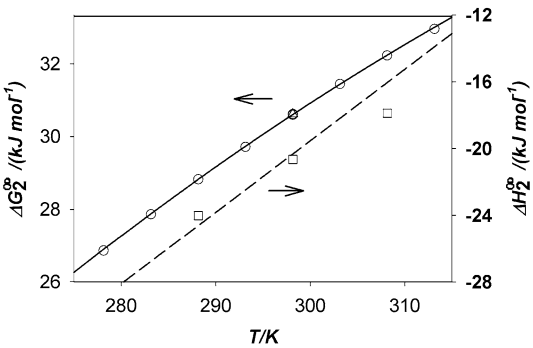

Fig. 5 Plot of ΔG_2^∞ and ΔH_2^∞ against temperature for SF_6 in water. ΔG_2^∞: *full line*, three-coefficient Valentiner equation; experimental points △ [22], ○ [5]. ΔH_2^∞: *dashed line*, three-coefficient Valentiner equation; □ [18]

7 Remarks for Some Gas + Water Systems

7.1 SF_6 and CF_4

The data of Mroczek [24] were not considered because they were obtained with the high-temperature technique. The values of ΔH_2^∞ for these two solutes were not satisfactorily represented by Eq. 6 when it was fitted simultaneously to calorimetric and solubility data, as shown in Fig. 5 for SF_6 (cf. Table 9). Hence, we have added tables with the values of the three coefficients when no ΔH_2^∞ values were considered, and they are given in Table 10 for SF_6.

Table 10 $SF_6 + H_2O$ system based on solubility data only

	$SF_6(0.011)$[a]	
	Coefficient	σ
a/kJ·(mol·K)$^{-1}$	3.6649	0.1463
b/kJ·mol^{-1}	−175.6262	6.4426
c/kJ·(mol·K)$^{-1}$	−0.52183	0.02188

[a]Overall σ

Table 11 $CF_4 + H_2O$ system based on solubility data only

	$CF_4(0.041)$[a]	
	Coefficient	σ
a/kJ·(mol·K)$^{-1}$	4.12009	0.35
b/kJ·mol^{-1}	−190.4615	15
c/kJ·(mol·K)$^{-1}$	−0.59277	0.052

[a]Overall σ

The same situation exists for CF_4 dissolved in water as shown in Table 11.

As expected, the overall standard deviations for both solutes are smaller when only solubility data were fitted, compared with the equation whose coefficients are reported in Table 9, but the polynomial cannot be used to satisfactorily represent the experimental calorimetric data.

7.2 Type E Systems

As already mentioned, for these systems there are no new solubility data, but calorimetric data do exist. When no new solubility data were reported, we relied on the solubility calculated with the equations published in the 1977 review [1]. Four different situations arose.

7.2.1 Type Ea

In the case of the solutes C_2H_2, C_2H_4 and $C(CH_3)_4$, no new solubility data have been published but calorimetric data have been reported. These data were found to be within 10% of those calculated from the temperature dependence of the solubility [1]. For these systems we recommend using the fitting equations given in that reference. Nevertheless, we also give here the values of ΔH_2^∞ (298.2 K) determined experimentally for the three solutes: −14,62 kJ·mol^{-1} for C_2H_2 [15], −16.46 kJ·mol^{-1} for C_2H_4 [15], and −25.11 kJ·mol^{-1} for $C(CH_4)_4$ [15].

7.2.2 Type Eb

For these systems there are new sources reporting a large amount of calorimetric data and, because there are no new solubility data, we considered it convenient to use them together with the solubility data as calculated with the equations given in [1] and then fitted the complete set with Eq. 6. The procedure followed for these systems involved calculating, with the equations given in [1], as many equally separated points for ΔG_2^∞ over the experimental temperature range as were originally considered by Wilhelm et al. [1].

This procedure was used for the following gases: C_3H_8, n-C_4H_{10} and i-C_4H_{10}. For each of these three systems there are several important calorimetric studies for C_3H_8 [8, 15, 19] for n-C_4H_{10} [8, 15, 27] and for i-C_4H_{10} [15, 27].

For C_3H_6 and c-C_3H_6 there are no new solubility data and the difference of the values of ΔH_2^∞ obtained calorimetrically and those calculated with the temperature dependence of the solubility [1] is very large, so it was not considered convenient to fit the two types of data simultaneously. For the solubilities we recommend using those calculated with the equations given in [1]. We report here the experimental values for ΔH_2^∞: -21.64 kJ·mol^{-1} for C_3H_6 [15]; -23.26 kJ·mol^{-1} for c-C_3H_6 [15], which are found to be inconsistent with the temperature dependence of the solubility.

7.2.3 Type Ec

For the gases C_2F_6, c-C_4F_8 and H_2S there are new solubility data but they are of lower precision and no calorimetric data exist, and the coefficients are given in Table 9. For the solute c-C_4F_8, the value of σ was very small because there are only four data points to adjust the three parameters. For H_2S the solubility data for the low-temperature range reported by Lee and Mather [29] were extrapolated to zero gas partial pressure and then Henry's constant was calculated.

7.2.4 Type Ed

For the gases $CBrF_3$ and 1-C_4H_8 there are no solubility data, so we only give here the values of ΔH_2^∞(298 K) reported in the literature for each solute: -23.72 kJ·mol^{-1} for $CBrF_3$ [27] and -24.88 kJ·mol^{-1} for 1-C_4H_8 [15].

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