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Evaluation of Data on Solubility of Simple Apolar Gases in Light and Heavy Water at High Temperature

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The solubility data of apolar gases in light and heavy water over the temperature range covered experimentally have been evaluated, laying particular emphasis to the region above the normal boiling points of the solvents. The systems that have been included in this work are the inert gases and CH_4 in light water and heavy water, H_2, O_2, N_2, and C_2H_6 in light water and D_2 in heavy water. Data in the original sources have been brought to the same footing by calculating from the raw experimental data P, T, and x when they were not reported by the author. This step is considered necessary to assess critically the available sets of data. The temperature dependence of Henry's constants for all the binary systems have been expressed in terms of two different polynomial equations. The formulations presented are discussed and the limits of application given.

Key words: dissolution of gases; heavy water; Henry's constants; liquid–vapor equilibrium; thermodynamic properties; water.

Contents

List of Figures

List of Tables

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List of Symbols

k_H^∞:	Henry's constant
x:	Mole fraction of solute in the liquid phase
y:	Mole fraction of solute in the gas phase
V_i:	Partial molar volume of component i
ϕ_i^i:	Fugacity coefficient of component i
Subscripts:	1, solvent; 2, solute
Superscripts:	∞, infinite dilution; *, pure substance

1. Introduction

The knowledge of the solubility of simple apolar gases in light and heavy water over a wide temperature range is of great interest in physical chemistry. Furthermore, for geochemical and industrial processes in aqueous medium where liquid–vapor equilibrium exists, it is important to have a suitable method to describe the solubility of gases under very different temperature and pressure conditions. One particularly important example is the power industry which generates electricity through the steam–water cycle; in this case it is necessary to describe the distribution of various apolar gases (H_2, O_2, etc.) between the vapor and the liquid phases. For this reason the International Association for the Properties of Steam has sponsored this critical evaluation at the X International Conference for the Properties of Steam held in Moscow in 1984.

Previous reviews of the solubility of simple nonpolar gases in water at high temperature[1,2] have not included heavy water as a solvent. Moreover, new experimental data referring to the systems H_2- and N_2-H_2O covering temperatures above 573 K have indicated[3] the convenience of modifying the equation used to describe the temperature dependence of Henry's constant in order to obtain a more thorough and satisfactory description of the thermodynamics of the dissolution process. At the same time, the method used previously to evaluate the data and to calculate Henry's constants, which are the primary source for the thermodynamic description of these binary systems, has been considerably improved.

For these reasons we have considered it desirable to undertake a critical reassessment of the available data as a result of which it will be possible to describe the solubility of gases in light and heavy water up to 640 K and 20 MPa of gas pressure above the solvent vapor pressure.

2. Thermodynamic Description

The solubilities of gases in liquids are, to a first approximation, directly proportional to the solute pressure; moreover, the change of total pressure also affects the chemical potential of the solute (i.e., its solubility) through the partial molar volume of the gas in solution. On the other hand, the effect of temperature upon gas solubility is very large. As a consequence it is necessary to have a formulation capable of dealing with both variables, P and T, in order to be able to deal with all the conditions under which it is desirable to know the solubility of gases in water. From this point of view the use of infinite dilution as the reference (Henry) state is important because then it is possible to produce a formulation in terms only of the temperature through the use of Henry's constants, k_H^∞. The pressure dependence of the solubility may be calculated with a semiempirical perturbational procedure, which relies on the information obtained from solubility and the properties of the pure solvent.[3] As will be pointed out below, when the temperature of the solution approaches the critical temperature of the solvent (T_{cl}) it becomes increasingly difficult to separate the effect upon solubility of solute concentration (activity coefficients) from

that of total pressure (solute partial molar volume).

Equilibrium between the gaseous and liquid phases is the thermodynamic starting point for the description of the dissolution process. For the solute we have,

$$\mu_2(T,P,x) = \mu_2^\phi(T) + RT \ln f_2^H x$$
$$+ \int_{P_1^*}^{P} V_2^\infty dP = \mu_2^0(T) + RT \ln(y\phi_2 P). \quad (1)$$

The definition of Henry's constant k_H^∞ is,

$$\mu_2^\phi(T) - \mu_2^0(T) = RT \ln k_H^\infty$$
$$= -RT \ln \frac{f_2^H x_2}{y\phi_2 P} \exp \int_{P_1^*}^{P} \frac{V_2^\infty}{RT} dP. \quad (2)$$

The difference of solute standard chemical potentials given by Eq. (2) refers to the process of taking gas from an ideal gaseous mixture at partial pressure of 0.1 MPa, dissolving it in the liquid at infinite dilution and then taking the solution to $x = 1$ (in a virtual process), while the interactions of the gas molecule remain identical to those existing at infinite dilution.

In order to calculate k_H^∞ according to Eq. (2) it is necessary to know the activity coefficient of the gas in the liquid, f_2, and to perform the integration indicated in the right hand side of Eq. (2). The procedure employed in this work consists in assuming that the activity coefficients are close to unity because the actual solutions are very dilute and that the V_2^∞ term is pressure independent, hence

$$k_H^\infty(T) = \frac{y\phi_2 P}{x} \exp\left[-\frac{V_2^\infty(P - P_1^*)}{RT} \right]. \quad (3)$$

These assumptions may be justified[3] except close to the critical temperature of the solvent, where the solubility increases strongly and the partial molar compressibility of the solute is very large. To calculate k_H^∞ from the experimental value of the gas solubility and the total pressure over the system using Eq. (3), it is necessary to have a knowledge of the thermodynamic behavior of the gas phase, i.e., its composition and the fugacity coefficient of component 2. Only for a few of the systems surveyed in this work have the gas phase compositions in equilibrium with the saturated solutions been experimentally determined, moreover these values are not considered to be very reliable.[2] Consequently, in order to obtain k_H^∞, it is necessary to use also the condition of equilibrium for the solvent. Thus,

$$1 - y = \frac{(1-x)P_1^*\phi_1^*}{P\phi_1} \exp \frac{V_1^*(P - P_1^*)}{RT}. \quad (4)$$

The same comments made after Eq. (3) apply to Eq. (4). The actual procedure of calculation and the equation of state that have been employed are described in Appendix I.

3. Systems Surveyed and Method of Data Analysis

We have taken into consideration all the information of gas solubility data available in the literature for inert gases and CH_4 in light and heavy water, for H_2, N_2, O_2, CH_4, and C_2H_6 in light and for D_2 in heavy water above room tempera-

ture. It is important to summarize the guidelines followed in this survey. The experimental methods used to determine the solubility of gases in liquids at temperatures lower than their normal boiling points[4] are very different from those that may be employed to study the same systems at temperatures between the normal boiling point and the critical temperature of the solvent. Moreover, with the methods available at present the attainable precision close to room temperature is between one and two orders of magnitude higher than above the normal boiling point of the solvent. Consequently, it does not seem appropriate to mix data from both temperature regions. Battino and co-workers have carefully reviewed[5] [5a] the gas solubility data in light and heavy water up to 323 K and to 298 K, respectively. In order to describe the gas solubility also in the low temperature region we have adopted the values of k_H^∞ given in that review (see Appendix II). This procedure was employed for all the systems in light water and for Ar and CH_4 in D_2O. For the higher temperature range, which is the central objective of this work, the criterion used implied incorporating only data above 323 K for H_2O and 298 K for D_2O from those experimental studies which employed the methods designed for studies at high temperatures. This meant the exclusion of some low temperature–high pressure data of good quality.[6] Only those data reported in tabular form were considered in this work because the uncertainty is too large when data are retrieved from graphs and, moreover, it is not possible to recover the primary experimental information. This latter point conditions any critical evaluation of gas solubility in liquids over a wide temperature range, because the method of data treatment partially determines the value obtained for k_H. Thus, regarding the behavior of the gas phase, some authors consider that it is ideal; others make partial corrections for nonideality. When not available, we decided to recalculate the T, P, and x values from the numbers reported in each study and the particular procedure employed for data treatment. This was our starting point in order to consider all the data under the same footing. We have included all the sources and only rejected a few individual data as detailed in Appendix II.

The majority of the gas solubility data are reported for a single gas pressure at each temperature. For those studies which had measured gas solubility at different pressures and at the same temperature, we extrapolated graphically the solubility value to $P = P_1^*$, the solvent saturation vapor pressure. We proceeded thus because it is common to observe[2] that the reported pressure dependence of solubility is strongly influenced by each experimental set up and procedure employed.

The detailed thermodynamic procedure used to calculate k_H^∞ is mentioned in Appendix I. Table 1 summarizes the original sources of data considered for each system, maximum temperture of the data and number of points rejected in each source.

4. Temperature Dependence of Henry's Constants

In agreement with other authors we observed[2] that with a polynomial in powers of the reciprocal temperature we can

fit k_H^∞ from ambient temperatures to 523 K. That is,

$$\ln k_H^\infty = \sum_{i=0}^{N} \frac{A_{i+1}}{T^i} (1000)^i. \tag{5}$$

The resulting A_i coefficients and the percent standard deviation ($\sigma\%$) for each system are reported in Table 2. With the reported values of the coefficients and the temperature in K, Henry's constant results in GPa.

When this polynomial is used to calculate the isobaric heat capacity of dissolution, C_{p2}^∞, the calculated values start diverging above 423 K from those obtained directly by calorimetry.[3,7,8] Furthermore, Eq. (5) is unable to predict the divergence to $+\infty$ of C_{p2}^∞ and to $-\infty$ of $d\ln(k_H^\infty)/dt$ when T approaches T_{cl}.[9] This behavior influences the temperature dependence of k_H^∞ above 573 K as we have recently verified[3] with the system H_2– and N_2–H_2O[10] which could not be properly described within experimental uncertainty by Eq. (5). For these reasons we also have fitted the data to,

$$\ln k_H^\infty = \frac{B_0}{T}(T_{cl} - T)\ln\left(\frac{T_{cl} - T}{T_{cl}}\right) + \sum_{i=0}^{N} \frac{B_{i+1}}{T^i} (1000)^i. \tag{6}$$

The best value of B_0 was between 0 and -4 for almost all the systems studied (Kr–H_2O had a positive best fit B_0 and C_2H_6–H_2O a value > -4). The standard deviation of the fit was relatively insensitive to changes in B_0 over a wide range of value. To avoid a positive value of B_0 for Kr–H_2O which would lead to a $-\infty$ divergence of C_{p2}^∞ when T approaches T_{cl}, we have preferred to make $B_0 = -1.0$ for all the systems, a choice which affords a uniform treatment and which does not affect the standard deviation of the fitting procedure. In Eq. (6) the value 647.3 K was used for T_{cl}. Coefficients for this equation are given in Table 3. Units are GPa for Henry's constant and K for the temperature. The percent standard deviation of the data ($\sigma\%$) is similar to that obtained with Eq. (5), but the advantage of Eq. (6) is that it has no conceptual limitations in the maximum temperature at which it can be used.

A general feature of the gas solubility data in liquid water well above the normal boiling point of the solvent, is that for each gas water system the scatter of the k_H^∞ values obtained in different laboratories is much greater than the reproducibility and standard deviation obtained in some single sources. This is due to the particularly difficult conditions of the experimental work. As a consequence, the overall standard deviation of the fitting for each binary system results in the order of magnitude of the uncertainty quoted in, or that can be attributed to, the original source with the greatest experimental scatter.

The formulations given in the present work should preferably be used inside the temperature interval of the actual data (see Table 1). This is especially important for any calculation to be done based on Eq. (5).

Appendix II gives details regarding the fitting procedure that has been employed and the criterion for data rejection.

Table 4 gives values for Henry's constant at some selected temperatures calculated with Eqs. (5) and (6) for all the systems evaluated in this work. As would be expected, differ-

Table 1. Sources of data of solubility of gases in light and heavy water surveyed in the present work

System	T/K[a]	Sources[b].
$He-H_2O$	588.7	W35(2:1), P52(3:3), S62(3:2), G72(2:0), P78(4:4)
$Ne-H_2O$	543.4	P78(5:1), C82(7:6)
$Ar-H_2O$	568.4	P78(10:2), C82(7:6)
$Kr-H_2O$	525.6	P78(4:2),C82(6:5)
$Xe-H_2O$	574.8	S56(4:4),P78(5:5),C82(6:6)
CH_4-H_2O	633	M36(4:4),C51(7:6),S72(7:4),C82(6:4),C82a(10:6)
$C_2H_6-H_2O$	473	C50a+C50b(4:1),C84(13:13)
H_2-H_2O	636	W34(2:2),I34(6:6),P52(4:4),S56(3:3),A86+88 (25:25)
N_2-H_2O	636	G31(4:4),W33(2:2),S34(14:14),P52(2:2),O70(3:3) A86+A88 (32:32)
O_2-H_2O	616	P52+P53a+S56(8:7),C82a(12:11)
$He-D_2O$	323-553	S62(6:6)
$Ne-D_2O$	293-550	C82(9:9)
$Ar-D_2O$	583	C82(14:14) (14:13) [c]
$Kr-D_2O$	293-523	C82(6:6)
$Xe-D_2O$	295-574	S56(4:4),C82(5:5)
D_2-D_2O	436-575	S56(3:3)
CH_4-D_2O	517	C82(8:8)

[a]This column gives the experimental range covered in this survey, or the maximum temperature of the data when the low temperature region was taken from Reference 5.

[b]The identification of the source is followed by (m:n), m being the number of experimental points in the source and n the number of experimental points finally included in the evaluation.

[c]In order to fit this system with Eq. (5) one point had to be eliminated to obtain a standard deviation comparable to that of Eq. (6).

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Table 2. Coefficients of Equation (5)

System	A_1	A_2	A_3	A_4	A_5	σ [a] %	T_m^b
He-H_2O	− 7.1725	5.9734	−0.9038			5.9	588.7
Ne-H_2O	− 5.9825	5.5176	−0.8886			3.2	543.4
Ar-H_2O	− 7.8972	7.0178	−1.2649			2.7	568.4
Kr-H_2O	− 7.5642	6.8773	−1.3047			2.9	525.6
Xe-H_2O	− 9.3604	7.9654	−1.5167			12.9	574.8
O_2-H_2O	−15.9766	15.7951	−4.3331	0.3502		5.0	616.0
CH_4-H_2O	−18.5223	17.7956	−4.8318	0.3856		3.3	633.0
C_2H_6-H_2O	−22.0320	21.0292	−5.6800	0.43658		2.7	473.0
H_2-H_2O	−46.0050	64.8729	32.9118	7.6094	−0.6673	10.8	636.0
N_2-H_2O	−55.5386	77.9340	−39.9781	9.2813	−0.82261	8.9	636.0
He-D_2O	− 7.8471	6.7707	−1.1146			2.9	553.0
Ne-D_2O	− 5.8356	5.4582	−0.8936			1.8	550.0
Ar-D_2O	−11.6961	11.1069	−2.6747	0.1550		2.7	583.0
Kr-D_2O	− 7.6687	6.9270	−1.3124			2.0	523.0
Xe-D_2O	−21.0042	20.9957	−6.2742	0.5673		6.0	574.0
CH_4-D_2O	− 8.7142	7.6882	−1.3988			1.2	517.0
D_2-D_2O	− 3.3351	2.0788				12.4	575.0

[a] σ is the standard deviation of the data to the fit (in %)

[b] T_m is the maximum temperature of the data. Eq. (5) can be recommended for use up to 573 K

Table 3. Coefficients of Equation (6)[a]

System	B_1	B_2	B_3	B_4	B_5	σ[b] %
He-H$_2$O	-6.4859	5.2327	-0.8086			6.5
Ne-H$_2$O	-5.3238	4.7936	-0.7959			2.1
Ar-H$_2$O	-7.1874	6.2632	-1.1676			1.5
Kr-H$_2$O	-7.0173	6.2204	-1.2220			4.0
Xe-H$_2$O	-8.7307	7.2588	-1.4265			11.8
O$_2$-H$_2$O	-13.3190	12.8557	-3.4516	0.2592		4.7
CH$_4$-H$_2$O	-15.5767	14.5624	-3.8519	0.2838		2.5
C$_2$H$_6$-H$_2$O	-20.6180	19.3949	-5.2453	0.3956		2.7
H$_2$-H$_2$O	**-38.4512**	**53.4846**	**-27.4317**	**6.3522**	**-0.5590**	**10.6**
N$_2$-H$_2$O	-47.7453	66.7623	-34.2820	7.9705	-0.7094	8.4
He-D$_2$O	-6.6883	5.6197	-0.9357			2.5
Ne-D$_2$O	-4.9291	4.5256	-0.7600			1.8
Ar-D$_2$O	-8.3908	7.2331	-1.3623			2.0
Kr-D$_2$O	-6.8494	6.0574	-1.1901			1.7
Xe-D$_2$O	-18.2951	17.9143	-5.3081	0.4622		6.0
CH$_4$-D$_2$O	-8.1286	6.9889	-1.3062			1.1
D$_2$-D$_2$O	-2.8180	1.6148				10.0

[a]Equation (6) can be recommended for use up to 635 K

[b]σ is the standard deviation of the data to the fit (in %)

J. Phys. Chem. Ref. Data, Vol. 18, No. 3, 1989

1237

Table 4. Calculated values of $\ln(k_H^\infty/\text{GPa})$ from Eqs. (5) and (6)

T/K	He-H_2O a	b	Ne-H_2O a	b	Ar-H_2O a	b	Kr-H_2O a	b
323.15	2.658	2.657	2.583	2.582	1.707	1.707	1.224	1.224
373.15	2.345	2.361	2.422	2.438	1.825	1.843	1.496	1.508
423.15	1.896	1.926	2.094	2.121	1.623	1.655	1.402	1.420
473.15	1.415	1.445	1.710	1.736	1.285	1.318	1.143	1.154
523.15	0.943	0.954	1.318	1.323	0.896	0.910	0.815	0.800
573.15	0.498	0.463	0.939	0.897	0.497	0.466	0.463	0.396
623.15	---	-0.044	---	0.447	---	-0.016	---	-0.055

T/K	Xe-H_2O a	b	O_2-H_2O a	b	CH_4-H_2O a	b	C_2H_6-H_2O a	b
323.15	0.765	0.765	1.785	1.785	1.704	1.705	1.589	1.587
373.15	1.093	1.108	1.973	1.964	1.888	1.879	1.934	1.933
423.15	0.993	1.019	1.773	1.768	1.637	1.633	1.705	1.705
473.15	0.700	0.772	1.357	1.364	1.146	1.158	1.163	1.161
523.15	0.324	0.324	0.829	0.845	0.533	0.559	0.461	0.445
573.15	-0.080	-0.128	0.251	0.261	-0.134	-0.107	-0.313	-0.365
623.15	---	-0.628	---	-0.379	---	-0.827	---	-1.240

T/K	H_2-H_2O a	b	N_2-H_2O a	b	He-D_2O a	b	Ne-D_2O a	b
323.15	2.040	2.040	2.399	2.399	2.451	2.435	2.498	2.491
373.15	1.924	1.929	2.404	2.409	2.310	2.283	2.374	2.372
423.15	1.710	1.708	2.205	2.202	1.944	1.928	2.073	2.083
473.15	1.359	1.353	1.806	1.799	1.497	1.493	1.709	1.724
523.15	0.847	0.848	1.200	1.200	1.035	1.027	1.333	1.337
573.15	0.189	0.198	0.410	0.419	0.584	0.549	0.967	0.934
623.15	---	-0.593	---	-0.531	---	0.048	---	0.504

T/K	Ar-D_2O a	b	Kr-D_2O a	b	Xe-D_2O a	b	CH_4-D_2O a	b
323.15	1.655	1.640	1.199	1.193	0.696	0.701	1.682	1.684
373.15	1.843	1.841	1.470	1.468	1.120	1.118	1.843	1.851
423.15	1.660	1.656	1.372	1.389	1.060	1.058	1.642	1.655
473.15	1.294	1.294	1.109	1.120	0.700	0.703	1.287	1.291
523.15	0.844	0.850	0.777	0.773	0.166	0.173	0.871	0.850
573.15	0.364	0.362	0.422	0.377	-0.459	-0.463	0.442	0.369
623.15	---	-0.654	---	-0.066	---	-1.179	---	-0.150

Table 4 - continued

T/K	D_2-D_2O		
	a	b	
223.15	3.098	2.873	
273.15	2.236	2.141	
423.15	1.578	1.560	
473.15	1.058	1.078	
523.15	0.639	0.661	
573.15	0.292	0.280	
623.15	---	-0.099	

$\ln$ (k_H^∞/GPa) calculated from Eq. (5)

$\ln$ (k_H^∞/GPa) calculated from Eq. (6)

ences in values of Henry's law constant calculated from Eqs. (5) or (6) increase as the temperature increases. Generally, the differences are within the fitting standard deviation.

Conclusions

The overall standard percent deviation ($\sigma\%$) reported in Tables 2 and 3, reflects the fact that when data from several laboratories are considered together, the deviations in k_H^∞ are larger than the best attainable experimental precision (1%-2%). Nevertheless, it was considered desireable to incorporate data from as many sources as possible, minimizing points to be rejected. Points were rejected only in the cases mentioned in Appendix II.

In a previous partial survey of gas solubility[2] we had discussed the possibility of employing for all gases a general formulation having two system-specific parameters: the temperature of minimum solubility and the corresponding value of Henry's constant. However, as we can not predict the values of these parameters for different gases in water and as the temperature range in which such general formulation may be employed is limited because it does not give the correct tendencies, neither in ΔC_{p2}^∞ nor in $d \ln(k_H^\infty)/dT$, we have decided not to proceed further with it.

We suggest that use of Eq. (5) between 273 K and the maximum temperature given for each system in Table 1, but never exceeding 573 K; Eq. (6) may be used up to 635 K. However, due to the fact that many data sources have been considered in this survey for each system, the percent standard deviation of k_H^∞ shown in Tables 2 and 3 does not reflect an appreciable difference between the performance of Eqs. (5) and (6). The systems where differences could be expected, because there are data above 573 K, are N_2-, H_2,

CH_4- and to some extent O_2-H_2O. At the same time they are the ones with the greatest number of different sources and, therefore, more severely affected by the differences between them. Nevertheless we consider it convenient to use the suggested temperature ranges for each equation, because thermodynamic quantities derived from Henry's constants are strongly affected by the particular equation employed to fit the temperature dependence of k_H^∞.

6. Acknowledgments

a) To whom correspondence should be addressed.

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Appendix I. Procedure for the Calculation of Henry's Constants

In order to compare data from different sources it was necessary to retrieve from the reported solubility data the raw experimental information, i.e., T, P, and x, which is the input of our data treatment. In order to achieve this goal we have employed, if it was necessary, the calculation procedure described by each author to recalculate the data. To obtain k_H^∞ with Eqs. (3) and (4) from the complete set of raw data it is necessary to have an equation of state for the gas phase and a value of V_2^∞ in order to account for the effect of pressure on the gas solubility expressed by the exponential term in Eq. (3).

1. Equation of State

From the relatively large number of cubic equations of state available in the literature, we have chosen that of Peng and Robinson[11] for the description of the behavior of the gas phase binary mixture consisting of water vapor and a nonpolar gas. This choice was based on the facts that this equation is known to describe adequately the vapor–liquid equilibrium in H_2O–apolar gas systems[12] and that it is a simple equation. It is possible to use this equation over all of the temperature range covered by the present survey. It is worth pointing out that the difference introduced by the nonideal behavior of the gas phase in equilibrium with the saturated solution, that is the value of y calculated from Peng and Robinson's equation never differed from y for ideal behavior more than 20%. This is taken to imply that in order to obtain k_H^∞ within experimental uncertainty (1%–2%) any of the equations of state reputed as good ones could be used. On the other hand, it should be pointed out that the common practice of correcting the solute partial pressure with ϕ_2 (i.e., calculate its fugacity) without taking into account the corresponding change in y (gas phase composition), should be strongly discouraged since the resulting effect in k_H is usually worse than the simpler assumption of ideal behavior of the gas phase.

For binary gas mixtures, Peng and Robinson's equations of state requires an interaction parameter δ_{ij} which is temperature and pressure independent. The full equation is,

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)}, \quad (\text{I.1})$$

where each symbol has the usual meaning. For mixtures the parameters and b becomes[12]:

$$a(T) = \sum_i \sum_j y_i y_j (1 - \delta_{ij})(a_i a_j)^{1/2}, \quad (\text{I.2})$$

$$b = \sum_i y_i b_i.$$

Based on its temperature and density independence we have determined δ_{ij} from a generalized reduced second virial coefficient[13] obtained from the behavior of several binary mixtures of apolar gases and water vapor at temperatures below 523 K. Although it was possible to perceive a slight temperature dependence of δ_{ij} qualitatively the same for all the systems, a mean value was adopted for all the temperature range. As the values found were about the same for the majority of the systems, we used $\delta_{ij} = 0.50 \pm 0.05$. Exceptions are He–$H_2O$, $\delta_{ij} = 0.80 \pm 0.03$, N_2–H_2O, $\delta_{ij} = 0.45 \pm 0.12$ Ne's $a(T)$ approaches zero at the reduced temperatures of this work; for Ne–H_2O we have taken $\delta_{ij} = 0.50$. The parameters in Eq. (1) for the pure components were obtained from the literature.[14]

2. Effect of Pressure upon Gas Solubility

There are only two types of gas solubility studies: (i) those which have measured isothermally the solubility at various pressures, usually quite large ones, and (ii) those which measured only a few points at the same temperature, usually at a single pressure. The ones in the (i) type have usually been measured at quite large pressures. We have verified that the reported variation of solubility with pressure is strongly dependent on the author and hence we believe that, with some notable exceptions,[6] the reported dependence of $d [\ln(k_H^\infty)]_T$ on pressure is mainly an artifact of the experimental procedure employed. Hence, in order to obtain k_H^∞ a direct extrapolation of the reported data to $P = P^*$ was graphically performed.

When very few (in general only one) P, x data for a given temperature were available, we have obtained V_2^∞ as described below and calculated directly k_H^∞ with Eqs. (3) and (4).

2.1. Calculation of V_2^∞

It has been shown that by using a semiempirical perturbation method it is possible to describe the thermodynamics of dissolution of gases in H_2O and D_2O over a wide temperature range. Employing the value of the hard-sphere equivalent diameter of the solute at each temperature, and the properties of the pure solvent, it is possible to calculate perturbationally V_2^∞ as a function of temperature and pressure and with it the contribution of the exponential term appearing in Eq. (3).

Appendix II. Fitting Procedure Employed to Calculate the Temperature Dependence of Henry's Constants and Point Rejection Criteria.

The fitting procedure selected was a linear least-square method. We used a commercially available Harwell's Li-
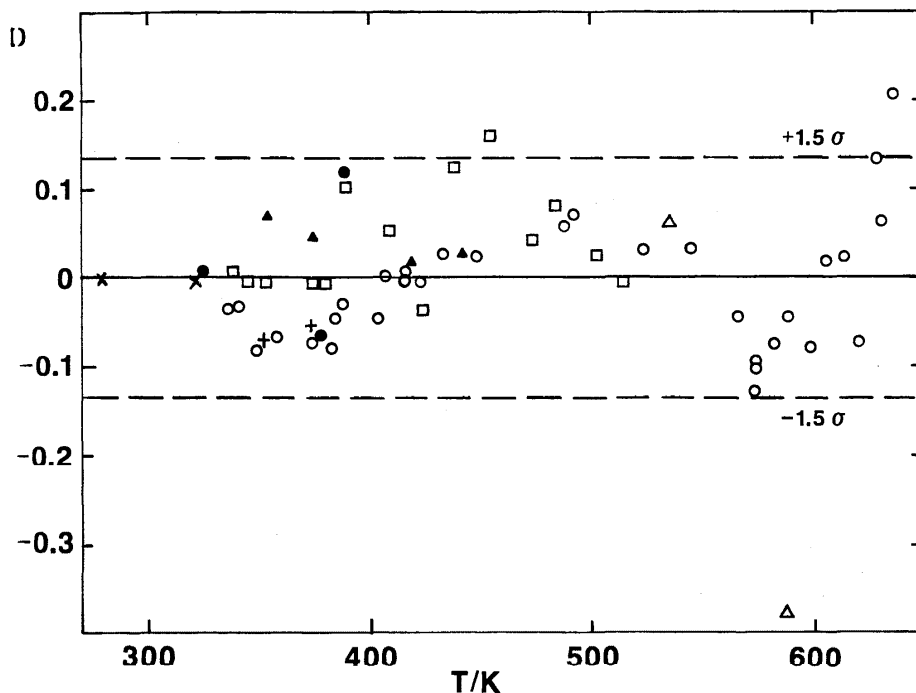
FIG. 1. Deviation plot for the system N_2-H_2O. $D = \Delta \ln (k_H^\infty/\text{GPa})$ as experimental minus calculated value from Eq. (5). Broken lines correspond to $\pm 1.5 \sigma$ value. The symbols are: $\times$, exact values from Ref. 5a; $\blacktriangle$, G31; $\square$, S34; $\bigcirc$, A88; $\bullet$, O70; $\triangle$, P52; $+$, W33.

brary subroutine, namely MA14AD, which provides coefficients parameters, their confidence interval, residuals, fitting standard deviation (σ), and variance–covariance matrix as output.

Each system was least-square fitted to Eqs. (5) and (6). The fit was anchored at two exact, zero residual, values of ln k_H^∞. In this way we produced a good overlap with higher precision data in the low temperature region, below 323 K. Solubility data at 278.2 and 322.2 K for light water systems and at 278.2 and at 298.2 K for the systems Ar– and CH_4–D_2O were taken from reviews of Battino and co-workers.[5, 5a]

The polynomial degree for Eqs. (5) or (6) was selected by looking for the minimum number of terms that gave a

standard deviation which could not be improved significantly upon addition of another term.

Once the degree of the polynomials was determined, each binary system was analyzed to proceed to a data point rejection. If we set an stringent criterion we ran the risk of rejecting valuable data. On the other hand if we set lenient limits we could retain spurious data that can blur any possible interpretation. Considering this and our own experience of data acquisition, we decided to take off points whose residual was larger than $\pm 1.5 \sigma$ (confidence interval 76%). Those points were only provisionally eliminated and the set of data was fitted agian.

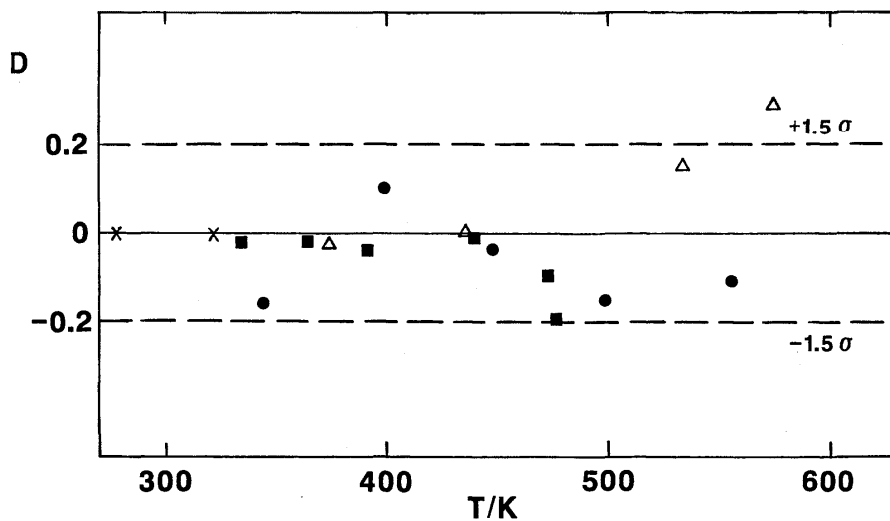If the new standard deviation of the fitting was not

FIG. 2. Deviation plot for the system Xe–H_2O. $D = \Delta \ln (k_H^\infty/\text{GPa})$ as experimental minus calculated value from Eq (5). Broken lines correspond to $\pm 1.5 \sigma$ value. The symbols are: $\times$, exact values from Ref. 5; $\blacksquare$, C82; $\bullet$, P78; $\triangle$, S56.
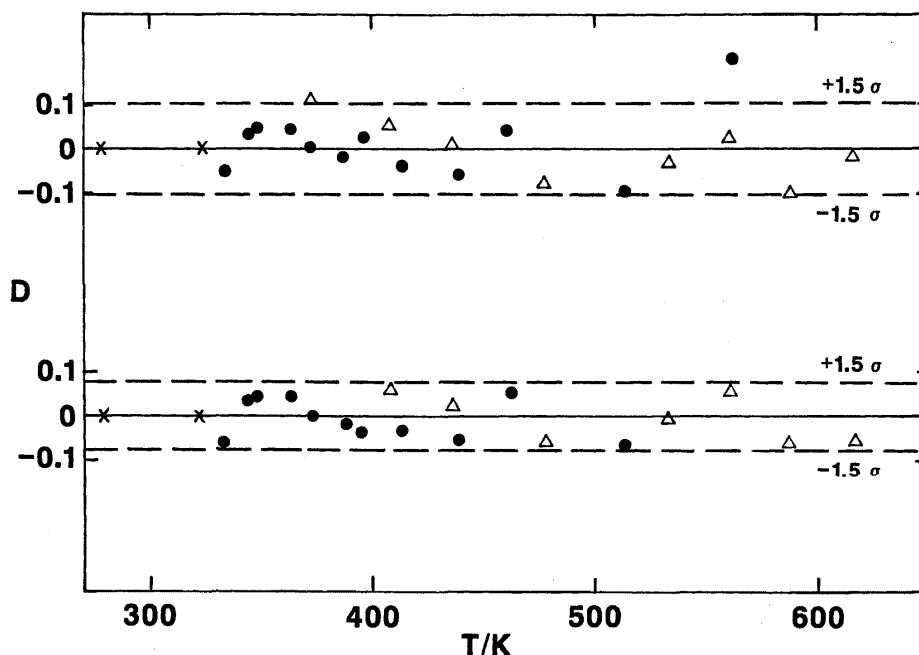
FIG. 3. Deviation plot for the system O_2-H_2O. $D = \Delta \ln (k_H^\infty/GPa)$ as experimental minus calculated value from Eq. (5). Broken lines correspond to $\pm 1.5\ \sigma$ value. The symbols are $\times$, exact values from Ref. 5a; $\bullet$, C82, $\triangle$, P52, P53a, S56.

found to decrease appreciably, the fitting was ended, the points were not rejected, and the polynomial coefficients for the complete data set are displayed in Table 2 and 3.

On the other hand, if the standard deviation of the fitting decreased appreciably, those points were definitively eliminated. The new output was screened again for points having a residual greater than $\pm 1.5\ \sigma$ and the whole procedure continued until the standard deviation did not decrease appreciably any more by points rejection. This was generally accomplished in one or two times. In all the systems studied the same experimental points deviated more than $\pm 1.5\ \sigma$ whether Eqs. (5) or (6) was used. As can be seen from Table 1, only very few points were definitely rejected.

In general the resulting standard deviation of the fitting for each system was of the order of magnitude of the greatest experimental uncertainty that was reported or that could be expected for the particular experimental method employed.

For Xe-H_2O and H_2-H_2O we found that σ is almost twice the expected value with all the experimental points scattered within $\pm 1.5\ \sigma$. This can be considered as a statistical disagreement between different sources which have employed quite different experimental approaches.

The only way to reduce σ in these cases is to remeasure the systems. This was done in our laboratory for the systems N_2-H_2O and H_2-H_2O.

Some systems require special comments:

The systems Ne-H_2O, Ar-H_2O, and Kr-H_2O have been measured only by two different sources, P78 and C82. P78's results differ from C82 as much as 20% for Ar-H_2O, and for Ne-H_2O the discrepancy is close to 30%. For Ne-H_2O they predict a completely different temperature dependence of Henry's constant from C82 or from the expected one.

The experimental techniques used in the sources are different. P78's method is synthetic and C82's is analytical sampling of the liquid phase. The discrepancies are very difficult to explain. We performed some experiments with the same set up as P78 decribes in his paper and our results showed us that without proper stirring conditions we could not obtain equilibrium in reasonable times. The determination of saturation pressure used by P78 can be objected to because it is a rather difficult extrapolation due to the steepness of the function plotted. This observations led us to the development of the modified method of measurement used in C84. So, in spite of the apparently good reproducibility observed for x, P78's method may be prone to lack of thorough equilibrium between the gas and the whole liquid phase. However, it is difficult to explain how this could lead to larger solubilities for Ar-H_2O. On the other hand, Ne-H_2O solubilities are smaller than C82.

Even at low temperatures, P78's data does not agree well with recommended values given in Battino's review.[5a] Although we have written to P78 about these problems and about the possibility of a printing mistake in the system Ne-H_2O, the authors never answered back.

We considered mainly only C82 data points for Ne-H_2O and Ar-H_2O because both sources cannot be reasonably fitted together.

P78's data are included for He-H_2O, Kr-H_2O, and Xe-H_2O whenever their residuals were inside $\pm 1.5\ \sigma$ of the fitting.

As an example of data treatment, Figs. 1, 2, and 3 give the deviation plot, as experimental minus calculated, for Henry's constant calculated from Eq. (5) for the systems N_2-H_2O, Xe-H_2O and O_2-H_2O, respectively, as a function of the temperature.

The system N_2–H_2O is an example of measurements done by many authors and with many experimental points. Although there are two points that scatter more than ± 1.5 σ as their residual is opposite in sign, their elimination will not greatly modify σ of the fitting and therefore all points in this system were considered.

Xe–H_2O is evenly scattered and no point elimination was done.

As can be seen in Fig. 3 for the system O_2–H_2O, the elimination of two points of two different sources, one at 373.15 K and the other at 561.15 K, produces a reduction of σ of the fitting from 7.5% to 5.0%. Those two points were eliminated and the fitting coefficients for the system without them are given in Tables 2 and 3.

In Table 4 calculated values of $\ln(k_H^\infty/\text{GPa})$ from Eqs. (5) and (6) at 50 K intervals from 323.15 to 623.15 K are given for all the systems evaluated.