Automated apparatus for gas solubility measurements

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Dedicated to Professor J. Simões Redinha on the occasion of his 80th birthday

Abstract

An automated apparatus based on the Ben-Naim–Baer and Tominaga *et al.* designs [A. Ben-Naim, S. Baer, Trans. Faraday Soc. 59 (1963) 2735–2738; T. Tominaga, R. Battino, H.K. Gorowara, R.D. Dixon, J. Chem. Eng. Data 31 (1986) 175–180] has been implemented for measurements of gas solubilities in liquids under atmospheric pressure and room temperatures. The uncertainty in the measurement of gas solubilities was estimated from the uncertainties in the directly measured quantities using the error propagation law. The accuracy of the experimental method was checked by measuring the solubility of carbon dioxide and nitrous oxide in water in the range $T = (290$ to 303) K, being found to be 0.6%. A precision of the same order of magnitude was achieved.
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1. Introduction

Ben-Naim and Baer have designed a volumetric gas solubility apparatus for slightly soluble gases in 1963 [1], which is considered a reference till nowadays. It is based on a direct reading of the change in volume of the gas during dissolution at constant pressure. A number of variations have been developed. One of these is the Tominaga *et al.* improved version [2] used in Battino's laboratory, which combined easy handling with automated data retrieval and was totally mercury-free.

In this work, we present a new design for solubility measurements around room temperature and atmospheric pressure that incorporates the best features of both apparatuses.

2. Experimental

2.1. Chemicals

Carbon dioxide and nitrous oxide were both Matheson products, Belgium, with a stated mole fraction purity of 0.995. The water (water G Chromasov) was obtained from Riedel and Häen, Germany.

2.2. Apparatus and solubility measurement

The experimental apparatus for solubility measurements is represented in figure 1. The principle of the method is to bring a measured amount of liquid into contact with a known volume of gas at a given temperature and pressure. After the equilibrium has been attained the change in the gas volume yields the amount of gas dissolved in the liquid and hence the solubility. The experimental procedure is similar to that described in detail in references [2,3].

The apparatus is housed in a water thermostat where the temperature is maintained constant by means of an Haake DC30 temperature controller, TC, Germany. The temperature is measured with a precision thermometer, T, graduated in 0.01 K, certified by NPL, UK, placed inside the bath. The temperature refers to the International Temperature Scale of 1990 (ITS 90). The level of the thermostat bath can be adjusted using an elevator, E.

The main parts of the apparatus are the equilibrium vessel, EQ, where the dissolution of the gas takes place; a gas

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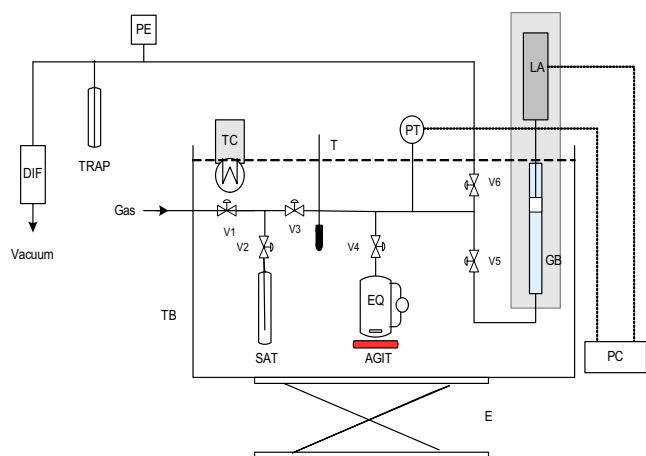 *E-mail address:* fonseca@eq.uc.pt (I.M.A. Fonseca).

FIGURE 1. Solubility apparatus: TB, thermostated bath; TC, temperature controller; T, thermometer; PT, pressure transducer; LA, linear actuator; PC, pressure controller; PE, Penning gauge; DIF, diffusion oil pump; TRAP, liquid N$_2$ trap; EQ, equilibrium vessel with connector; GB, gas burette; V1,…V6, high vacuum Teflon stopcocks; AGIT, magnetic stirrer; E, elevator.

burette, GB, which consists in a piston-cylinder arrangement; a saturation vessel, SAT; a pressure transducer, PT, from Honeywell, model PPT0015AWN2VA-A, USA, for total pressure readings; a linear actuator, LA, which moves the piston in the gas burette; and a pressure controller, PC. The stopcocks are in Teflon from J. Young, UK.

Before the dissolution procedure takes place, the total pressure is adjusted to *ca.* 0.1 MPa. This pressure acts as a reference value for the pressure controller which commands the linear actuator. As the gas dissolves, the pressure decreases and this is detected by PT. The linear actuator, LA, drives the piston down the cylinder to maintain the pressure constant at the reference value. The number of encoder pulses are counted and displayed and a conversion is made to determine the volume of gas displaced from the precision-bore tube that comprises that cylinder of the burette. This volume represents the volume of the gas dissolved.

In table 1, we present the main features of the apparatuses of Ben-Naim–Baer (BNB) and Tominaga *et al.* (TBGD) together with the apparatus implemented in our laboratory (FAF) for comparison purposes.

The initial, and perhaps the most important step in any gas solubility measurement, is to degas the liquid. There are a variety of ways to do this which have been discussed in several review articles. The method described by Battino *et al.* [4], which is by far the simplest and most efficient, was used in the apparatuses (TBGD) and (FAF). It takes place inside the vacuum line, and, in our case, inside the equilibrium vessel, which is more efficient and easy to use. This step lasts about 40 min and ends when the measured pressure equals the vapour pressure of the solvent at the equilibrium temperature. Since the vapour pressure is a

TABLE 1
Main features of gas solubility apparatuses and experimental procedures

Device or procedure	Ben-Naim–Bayer (BNB)[a](1963)	Tominaga *et al.* (TBGD)[b] (1986)	This work (FAF) (2006)
Degassing of solvent	Outside the apparatus	Inside the apparatus in the degassing vessel (method of Battino *et al.*[c])	Inside the apparatus in the equilibrium vessel (method of Battino *et al.*[c])
Equilibrium vessel	(400–800) cm^3 (calibrated volumes) (fixed position)	(26 to 1650) cm^3 (calibrated volumes) (fixed position)	(50 to 500) cm^3 (not calibrated, can be removed from the line during the experiment)
Determination of the solvent quantity	Volume measurement (cathetometer)	Volume measurement (cathetometer)	Mass measurement (balance)
Saturation of solvent (wet method)	Saturation vessel	Saturation vessel	Equilibrium vessel
Pressure control	Manual (presence of mercury)	Automatic by means of a micro-processor (mercury-free)	Automatic by means of a micro-processor or manual (mercury-free)
Determination of dissolved gas volume	By direct reading of the change of volume in a gas burette (uses mercury)	By means of a piston actuated stepping motor. The steps are counted and converted to determine the volume of dissolved gas	By means of a linear actuator. The number of encoder pulses are counted and converted in the volume of dissolved gas present (high vacuum, 10^{-3} Pa)
Diffusion oil pump	Nonexistent	Nonexistent	
Thermostated fluid	Water	Air	Water
Temperature control	0.03 K	>0.1 K	0.01 K
Stopcocks	In glass	In glass	In Teflon
Precision	0.2%	1 %	0.5%
Accuracy	Not stated	>1%	0.6%

[a] Reference [1].
[b] Reference [2].
[c] Reference [4].

property particularly sensitive to the presence of impurities, this procedure constitutes a good test of solvent purity.

Then the amount of solvent must be determined. As indicated in table 1, the equilibrium vessels have different volumes depending on the magnitude of the gas solubility. The larger vessels are used for less soluble gases. In the (BNB) and (TBGD) equilibrium vessels (with calibrated volumes), readings of the volume of solvent are determined using a cathetometer outside the thermostat. In (FAF), the equilibrium vessel is removed from the line, after the degassing procedure, to be weighed. This method of solvent determination is easier and more accurate.

The three apparatuses incorporate a saturation vessel which allows the use of the wet method [5]. The saturation procedure is similar in all of them. The gas to be dissolved is saturated with the solvent before the dissolution process takes place, which decreases the duration of this step [3]. However, as Fogg and Gerrard pointed out [5], the more soluble the gas, the greater the volume of solvent that condenses in the equilibrium vessel and the greater the error introduced in the solubility calculation by this effect. To avoid this error, the amount of solvent can be determined at the end of the experiment.

With regard to the control of pressure during the experiment, in the (BNB) device this control is manual. During the dissolution of the gas, one of the arms of the mercury manometer is continuously levelled by letting mercury into a gas burette [1]. In the other two apparatuses, both pressure control and measurement of the dissolved gas volume in a given amount of solvent are accomplished by a microprocessor. This makes possible the automatic operation of the system, the faster attainment of the equilibrium state and automatic data logging. The elimination of mercury is particularly relevant in the experiments involving gases reactive with this metal. During the dissolution step, there is the possibility of over saturation occurring, as Ben-Naim and Baer have referred [1]. They suggested that after equilibrium has been reached and a reading taken, the pressure should be reduced in order to expel some of the dissolved gas. Then, the re-establishment of pressure must lead to the former equilibrium, i.e., the final amount of gas dissolved must coincide exactly with the amount for the initial equilibrium. In our apparatus, this possibility can easily be examined, since control of pressure can also be made manually. Therefore, at the end of the experiment, after equilibrium has been reached and the final reading obtained, we can reduce the pressure inside the equilibrium vessel by raising manually the piston of the cylinder.

In the (BNB) apparatus, water was used as a thermostatted fluid, and the (TBGD) apparatus used air, to make the experimental procedure easier. We have decided to utilize water again, since it possesses higher thermal inertia which avoids temperature gradients inside the thermostat bath. To prevent some difficulties in handling the apparatus, we added an hydraulic system (elevator) capable of moving the bath up and down. This is used only twice during the experiment for removal of the equilibrium vessel.

The incorporation in the (FAF) line of a diffusion oil pump improves significantly the vacuum (10^{-3} Pa). The vacuum pressure is determined using a Penning gauge. In the (FAF) apparatus, the stopcocks are made from Teflon, waterproof, and therefore free of grease, which prevents the contamination of the solvent.

3. Results and discussion

3.1. Calculations

In the following text we use the subscript 1 to identify the solvent (water) and 2 for the solute (gas). In this work, the experimentally accessible quantities are the displaced volume in gas burette due to the gas dissolution, ΔV, the mass of solution, m_s, and the equilibrium pressure and temperature, P and T, respectively.

The amount of dissolved gas, n_2 (in moles), can be obtained from ΔV through the equation,

$$PV_{mix}^G/(RT) = 1 + B_{mix}RT/P, \qquad (1)$$

where V_{mix}^G represents the molar volume in the vapour phase and B_{mix} the second virial coefficient of the binary mixture, given by the expression,

$$B_{mix} = y_1^2 B_{11} + y_2^2 B_{22} + 2y_1y_2B_{12}, \qquad (2)$$

where y_1 and y_2 represent the mole fraction compositions in the vapour phase and B_{11}, B_{22} and B_{12} denote the second virial coefficients of pure components 1 and 2, and the second cross coefficient, respectively. Polynomial functions were fitted to the experimental second virial coefficients, taken from the Dymond and Smith [6] compilation.

Substituting in equation (1), $V_{mix}^G = \Delta V/n^G$, where n^G equals the total number of moles contained in the ΔV volume, one obtains

$$\Delta V/n^G = (RT/P) + B_{mix}. \qquad (3)$$

Equation (3) multiplied by the inverse of y_2 yields

$$n_2 = y_2P\Delta V/(RT + B_{mix}P). \qquad (4)$$

The mole fraction solubility of the solute, x_2, is obtained from

$$x_2 = n_2/(n_1 + n_2), \qquad (5)$$

where n_1 and n_2 represent the amount of solvent and solute in moles in the liquid phase, respectively.

The n_1 is directly obtained from, $n_1 = (m_s - n_2M_2)/M_1$, where M_1 and M_2 are the molar masses of the solvent and solute, respectively, neglecting the mass of the vapour phase inside the equilibrium vessel, which is an excellent approximation. Besides, we have verified that for the majority of data points, the assumption, $n_1 = m_s/M_1$, leads to the same solubility value.

Since we need to know y_2 to obtain n_2 from equation (4), this calculation requires an iterative procedure, similar to that presented by Rettich et al. [7]. The calculation begins with estimates of the compositions of the vapour and liquid

phases obtained from Raoult and Dalton laws. In the following iterations, these compositions are improved using equations (4) and (5) and also the following expression:

$$y_2 = 1 - (1 - x_2)\frac{P_1^*}{P}\frac{\varphi_1^{*,sat}}{\varphi_1^G} \cdot PC, \qquad (6)$$

which results from the thermodynamic condition of phase equilibrium. The φ_1^G is the fugacity coefficient of solvent in the vapour phase which is given by

$$\varphi_1^G = \exp\{(P/RT)[B_{11} + y_2^2(2B_{12} - B_{22} - B_{11})]\}, \qquad (7)$$

and $\varphi_1^{*,sat}$, represents the fugacity coefficient of pure solvent in saturation conditions obtained from,

$$\varphi_1^{*,sat} = \exp[B_{11}P_1^*/(RT)]. \qquad (8)$$

The P_1^* represents the vapour pressure of component 1 obtained from the Wagner equation [8] and the PC is the Poynting correction defined by the expression,

$$PC = \exp[V_1^{*,L}(P - P_1^*)/(RT)], \qquad (9)$$

where $V_1^{*,L}$ is the molar volume of the liquid taken from reference [8].

The calculation ends when convergence is obtained between two consecutive x_2 values.

The determination of Henry's constant, $H_{2,1}$ (T, P) is then straightforward:

$$H_{2,1}(T,P) = \varphi_2^G y_2 P/x_2, \qquad (10)$$

being φ_2^G, the fugacity coefficient of the solute in the vapour phase obtained from an equation similar to equation (7).

The solubilities found in this work were corrected to 101325 Pa partial pressure of the gas using Henry's law, since the literature values are referred to this pressure.

The experimental solubility data and the Henry's coefficients for CO_2 and N_2O in water, in the temperature range (290 to 303) K obtained in this work are shown in table 2 together with the literature values.

3.2. Evaluation of the quality of data

To evaluate the quality of the experimental data, Ben-Naim and Baer and Tominaga et al. indicated the precision (reproducibility) of the apparatuses as being of the order of 0.2% and 1%, respectively, (see table 1). There is no explicit reference to the accuracy of x_2 values in the first case. Tominaga et al. stated that they believe that their data have accuracy roughly of the same order of the precision [2]. However we have compared their experimental solubilities of several gases in CCl_4 at $T = 298.15$ K with reference literature data ($x_{2\,lit}$) presented also by the authors. We have calculated the deviations, $[100\,(|x_2 - x_{2\,lit}|/x_{2\,lit})]$, which vary in the range [0.5–5.5%]. This result can be considered a rough estimate of the accuracy of the experimental data, which fall off at the lower solubilities.

The uncertainty of our data was determined using the theory of errors. We have considered the following experimental uncertainties in the measured variables: tempera-

TABLE 2
Solubility of CO_2 and N_2O in water, expressed as mole fraction, x_2, at a partial pressure $P_2 = 101325$ Pa. The $H_{2,1}$ is the Henry coefficient

Solute	T/K	$x_2/10^{-4}$	$x_{2\,lit}/10^{-4}$	σ (%)[a]	$H_{2,1}$/MPa
CO_2	290.27	7.70	7.61	1.1	131.7
	291.49	7.36	7.34	0.3	137.7
	292.11	7.22	7.21	0.2	140.4
	293.39	6.90	6.94	0.6	146.8
	294.58	6.65	6.71	0.9	152.3
	295.15	6.66	6.60	0.9	152.1
	296.19	6.36	6.42	0.8	159.2
	297.19	6.19	6.24	0.9	163.8
	298.39	5.98	6.04	1.0	169.4
	299.37	5.89	5.89	0.0	172.0
	300.15	5.80	5.77	0.5	174.8
	301.10	5.61	5.63	0.3	180.5
	302.13	5.43	5.48	1.1	186.7
	302.93	5.35	5.38	0.5	189.5
N_2O	290.36	5.49	5.53	0.6	184.4
	291.36	5.38	5.36	0.4	188.4
	292.36	5.17	5.19	0.4	196.1
	293.30	5.03	5.04	0.2	201.5
	294.20	4.93	4.90	0.5	205.5
	295.40	4.71	4.73	0.3	214.9
	296.15	4.66	4.63	0.8	217.2
	297.25	4.49	4.48	0.3	225.6
	298.13	4.38	4.37	0.2	231.5
	299.07	4.28	4.25	0.7	236.6
	300.16	4.13	4.12	0.2	245.2
	301.15	3.97	4.01	1.0	255.0
	302.15	3.84	3.90	1.7	263.9
	303.13	3.81	3.80	0.0	266.3

[a] σ (%) = 100 ($|x_2 - x_{2\,lit}|/x_{2\,lit}$), where x_2 represents the solubility value found in this work and $x_{2\,lit}$ was obtained from reference [9].

ture, 10^{-2} K; pressure, 10 Pa; mass, 10^{-7} kg; volume of dissolved gas, 10^{-6} m³. This last uncertainty was calculated by taking into account the uncertainties in the internal diameter of the precision-bore tube of the burette (10^{-6} m) and the displacement of the piston (10^{-5} m). Using the error propagation law [10],

$$\Delta x_2 \approx \sum_i |\partial x_2/\partial v_i|\Delta v_i, \qquad (11)$$

where v_i represents the measured variables and Δv_i represents the experimental uncertainties, we have determined the x_2 uncertainty, $\Delta x_2 = 10^{-6}$ (or 0.1%). According to this result, we have reported our values with three significant figures (see table 2). The largest contribution to Δx_2 was the uncertainty in the volume of dissolved gas, $\Delta V = 10^{-6}$ m³.

Some of the measurements were repeated several times to evaluate the reproducibility of the data and a precision of the order of 0.5% was found.

The performance of the apparatus was tested by comparing our solubility data for carbon dioxide and nitrous oxide in water with reference literature data. These two gases were available in lecture bottles of high purity in our laboratory. A huge number of experimental studies have been conducted on the CO_2 solubility in pure water. In 1991, Carroll et al. [11] and Crovetto [12] compiled

and evaluated the quality of results for pressures below 1 MPa for this system. For the N_2O/H_2O system, the literature information is more scarce [9].

For the CO_2/H_2O system at the partial pressure of 101325 Pa, the data of Morrison and Billett [13], Murray and Riley [14], and Bohr [15] were classified as being the most accurate [11]. Thus, we have compared our results with the correlation presented by Wilhelm *et al.* [9], since this correlation was obtained using the experimental data of Morrison and Billett [13] and Murray and Riley [14] with an average absolute deviation of fitting of 0.54%. The correlation presented by Wilhelm *et al.* [9] for the N_2O/H_2O system has a relatively high average absolute deviation of fitting, 1.4%. In table 2, we compare our experimental solubility values with those obtained from the correlations. The average absolute deviation (AAD) defined as

$$AAD = (1/N) \sum_i 100(|x_2 - x_{2\,lit}|/x_{2\,lit}), \qquad (12)$$

where x_2 represents our data and $x_{2\,lit}$ those from the literature. The values obtained from the correlations are 0.65% and 0.52% for the systems CO_2/H_2O and N_2O/H_2O, respectively. The results are excellent for the CO_2/H_2O system. The comparison for the N_2O/H_2O is not totally conclusive due to the higher average absolute deviation of this correlation (1.4%). In any case, our values show good agreement with those obtained from the correlation.

In figure 2, we represent our experimental values and the correlations of Wilhelm *et al.* [9] for both systems. For the CO_2/H_2O system, we have included the data points of Bohr [15]. The AAD for these points, 1.33%, is surprisingly high.

The x_2 experimental uncertainty of our data estimated from error propagation law, 0.1%, is of the same order of magnitude as the average absolute deviation obtained from

the correlation, 0.65%, for the CO_2/H_2O system. The difference between the two percentages may be explained by the uncertainties that cannot be quantified in the error propagation law, such as the irreproducibility of the saturation of the gas with the solvent vapour, and uncertainties in the attainment of the equilibrium state, and also by the uncertainties of the literature data, which are responsible for the AAD of the correlation. We can conclude that there is still room for improvement in the experimental procedure.

4. Conclusions

A new automated apparatus for G/L solubility measurements was implemented which embodies the best features of two reference literature devices. Its performance was tested in the temperature range from 290 K to 303 K with high soluble gases, CO_2 and N_2O, in water. An accuracy better than 0.6% and a moderate precision of 0.5% were achieved.

In future work, the solubility of slightly soluble gases will be determined and we will extend the measurements to lower temperatures using an appropriate cooling unit.
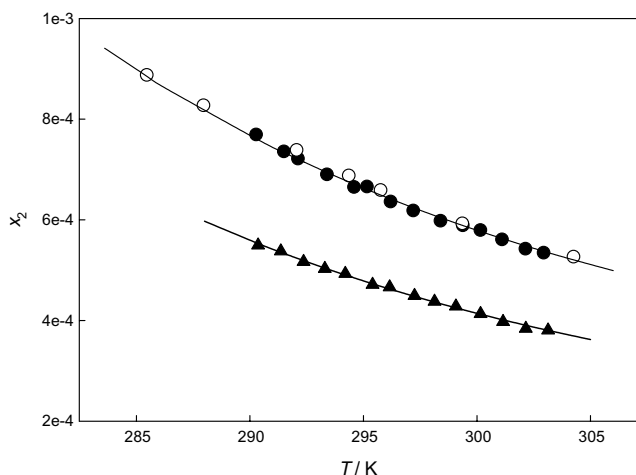
Acknowledgements

FIGURE 2. Plot of mole fraction against temperature to illustrate the solubility data of carbon dioxide (●) and nitrous oxide in water (▲) at the partial pressure of 101325 Pa obtained in this work. The curves represent the correlations given by Wilhelm *et al.* [9]. The data of Bohr [15] for CO_2/H_2O system over the temperature range from 290 K to 303 K are also included (○).

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