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Evaluation of Solubility Data of the System CO₂-H₂O from 273 K to the Critical Point of Water

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This critical review covers the existing literature on the solubility of CO_2 in water from 273 K to the critical temperature of the solvent (647 K). Results of the evaluation are expressed in the form of fitting equations for the infinite dilution Henry's constant, k^0 , as a function of the density of the solvent, and also as an explicit function of the temperature. The pressure effect on the solubility is considered in the formulation. Different equations of state were used for the description of the CO_2 -II₂O vapor phase and the effects on the calculated Henry's constant values are analyzed. The "best" solubility estimates are presented in smoothed tabular form.

Key words: CO_2 dissolution in water; solubility; Henry's constant; high temperature CO_2 solubilities in water.

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List of Symbols

Subscri	pts: 1: solvent, 2: solute, c: critical.
Superso	cripts: 0: infinite dilution, *: pure substance, g:
vapor p	hase, liq: liquid phase, s: saturation.
$a_{v,x}$	second derivative with respect to the vol-
	ume and composition of the Helmholtz
	free energy
k	Henry's constant
х	mole fraction of solute in the liquid phase
у	mole fraction of solute in the vapor phase
B_{12}	second cross virial coefficient

ρ

c_{112}, c_{122}	third virial coefficients
Cp_2	partial molar isobaric heat capacity for
	the solute
K _D	distribution coefficient
D	total pressure
R	gas constant
Г	Kelvin temperature
Γ#	reduced temperature, T/T_{1c}
V	molar volume
V_{i}	partial molar volume of <i>i</i>
Z	compressibility factor, PV/RT
Greek sym	bols:

1. Introduction

The solubility of CO_2 in H_2O is of great importance in nany different fields. At temperatures between 273 and 315 K it plays an essential role in biochemistry and biotechnology. At higher temperatures it becomes important to geohemistry, power plant water chemistry, industrial steamwater cycling, and engineering design. Also, a consistent set of evaluated data can be used as a test for predictions from nodels of aqueous solutions.

1.1. Background

Because of its natural abundance and biological imporance the solubility of CO_2 in water at low temperatures has been the subject of much research since as early as 1855. One of the pioneers in gas solubility research who defined and gave his name to a measure of solubility, Bunsen,¹ measured CO_2 solubilities in water from 4 to 22 °C in 1855. Also, some of the apparatus designed for measuring gas content in biological fluids, such as blood and plasma, that are still in use 10wadays, were tested and developed by measuring the solubility of CO_2 in water: see Van Slyke² and Van Slyke and Neil.³

This system has previously been considered in the review by Wilhelm *et al.*⁴ In this review only three sources for he system CO_2 -water from the existing low temperature lata were considered. The sources have almost no temperature overlap among them. These were the data of Morrison and Billet,⁵ Murray and Riley,⁶ and Weiss.⁷

The system CO_2 -heavy water at low temperature has no new measurements or data sources other than those already considered in the review by Wilhelm *et al.*⁴ and will not be reanalyzed here.

At high temperature there exists one set of measurenents on CO_2-D_2O from 303 to 473 K, Kapitanov *et al.*⁸ Unfortunately it is not possible to determine from the availible translation of this paper the temperature at which the lensity of the solvent was measured. Without this informaion the mole fraction of the dissolved gas, *x*, cannot be calulated. Thus the system CO_2-D_2O will not be evaluated at high temperatures.

1.2. Scope

Due to the importance of the system CO_2 -H₂O, a critiial evaluation and a representation of the temperature debendence of the existing solubility data from 273 K to the initial point of water and at pressures up to 20–30 MPa ibove the solvent vapor pressure is presented.

- molar density
- δ_{ij} mixture interaction parameter of Peng and Robinson
- ϕ_i fugacity coefficient in the gaseous mixture of component *i*
- γ^{H} activity coefficient in the liquid phase on the scale defining ideality by means of Henry's law
- γ^{R} idem but defining ideality by means of pure solvent behavior or Raoult's law

Mathematical notation:

ln base *e* logarithm, exp: exponential

In order to evaluate effectively the different sources, the data treatment must be carried out on the same basis for all sources. Thus every source of data has to be first reduced to the same raw experimental information, i.e., temperature, T, total pressure, P, and dissolved gas mole fraction, x, before any thermodynamic calculation can be started. This is strictly unavoidable for the high-temperature sources because the thermodynamic expression of the solubility depends on the raw experimental data and on the way of considering the system's nonideality. At low temperatures and pressures the nonideality of the systems is small and it would be absolutely necessary to account for nonideality only when dealing with very precise experimental data.

The saturation solubility will be characterized by the two phases' Henry's constant, k^{0} .

As the precision of the low-temperature solubility measurements is greater, by a factor of 3 or more, than that for measurements at high temperature, each set of data will be considered and evaluated separately.

The reevaluated low-temperature solubilities are compared with those from Wilhelm $et al.^4$

2. Thermodynamic Treatment

The concept of saturation gas solubility implies that a system is considered in which there are two coexisting phases in equilibrium. Usually the solubility data experimentally available are pressure, temperature, and concentration of the gas in the liquid, at equilibrium conditions. The concentration of the gas in the vapor phase is rarely an experimentally available datum.

The thermodynamic conditions for a binary liquid-vapor equilibrium in terms of Henry's constant have been presented, see O'Connel,⁹ and Alvarez *et al.*,¹⁰ and will therefore not be given here.

From the equality of the chemical potentials of the solute in the vapor and liquid phase the Henry's constant, k^{0} , can be defined as:

$$k^{0} = \left(\frac{\gamma P \phi_{2}}{\gamma_{2}^{H} x}\right) \exp \int_{P_{\uparrow}^{+}}^{P} \left(\frac{-V_{2}}{RT}\right) dP.$$
(1)

From the equality of the chemical potentials of the solvent in the liquid and the vapor phase, it follows that

$$(1-y) = \frac{\left[\gamma_1^R (1-x) P_1^* \phi_1^* \exp \int_{P_1^*}^P (V_1/RT) dP\right]}{(P\phi_1)}, \quad (2)$$

where the symbols (see list) have the usual meaning. In order to calculate k^0 from the experimental data usually avail-

able, namely P, T, and x, Eqs. (1) and (2) have to be solved simultaneously. The common assumptions for low temperatures and low total pressures and concentrations are that the activity coefficients γ_2^H and γ_1^R equal unity and that the partial molar volume, V_2 , equals the infinite dilution partial molar volume, V_2^0 independent of pressure. These assumptions will be discussed and justified below.

The necessary fugacity coefficients for the vapor phase mixture, ϕ_i , and for pure water, ϕ_i^* , can be calculated once an equation of state, EOS, is chosen to represent the vapor phase. To assess the sensitivity of the derived Henry's constant to the choice of an EOS the following equations were selected: a three coefficient-virial EOS in densities (*Vi*); Peng and Robinson's¹¹ mixture EOS (PR); Gibbons and Laughton's¹² equation(G); and Wormald and Lancaster's¹³ equation (W).

Up to about 500 K all of the EOS gave variations of about 1.5% or less in the calculated values of k^{0} . For details on the EOS, calculation procedures, and a discussion on the selection procedures, see Appendix I.1.

Once an EOS is selected, Eq. (2) is solved for the composition of the vapor phase, y, by an iterative procedure described elsewhere (see Crovetto *et al.*¹⁴)

The explicit pressure dependence of the solubility can be accounted for either by using information on experimental partial molar volumes or by semiempirical perturbational methods (see Fernández Prini and Japas.¹⁵) Details about the treatment of the pressure dependence are given in Appendix I.2.

The assumed values of the activity coefficients and the partial molar volumes must be reviewed very carefully near the critical point of the solvent. See Japas and Levelt Sengers.¹⁶ As these authors demonstrate, k^0 does exist and has a finite value at the critical temperature of the solvent.

A useful quantity in solubility and liquid/vapor equilibria is the isothermal distribution coefficient, K_D , defined as

$$K_D = y/x. \tag{3}$$

The infinite-dilution coefficient, K_{D}^{0} , is defined as

$$K_D^0 = \lim_{x \to 0} y/x, \tag{4}$$

and can be calculated from the same set of equations and assumptions already presented as

$$K_D^0 = k^0 / (P_1^* \phi_2^0), \tag{5}$$

where ϕ_2^0 is calculated from the selected EOS. In principle K_D^0 will be known with the same precision as k^0 but the effect of the selected EOS on the values of K_D^0 and k^0 , respectively, will be different.

Recently Japas and Levelt Sengers¹⁰ predicted the limiting asymptotic thermodynamic behavior for k^0 and K_D^0 and their temperature dependence near the critical temperature of the solvent. They demonstrated that asymptotically as $T \rightarrow T_c$ of the solvent the following linear correlations will apply:

$$T\ln(k^{0}/f_{1}^{*}) = A + B(\rho_{1}^{\text{siq}^{*}} - \rho_{c1}).$$
(6)

$$T \ln K_D^0 = 2B(\frac{hq^*}{\rho_1} - \rho_{c1}),$$
 (7) or KD

where

$$B(R\rho_c^2) = \left(\frac{\partial P}{\partial x}\right)_{V,Tc} \equiv -a_{V,x}^c.$$

The quantity $a_{V,x}^{c}$ is the second derivative of the Helmholtz free energy with respect to the volume and the concentration. This relevant derivative can be related to experimentally measurable initial critical-line slopes of the dilute solution and the pure solvent. (See Japas and Levelt Sengers.¹⁶) The strictly asymptotic Eq. (7) will be labeled KD for future reference. The fact that K_{D}^{o} must equal unity for $T = T_{c}$, provides a valuable clue to whether the asymptotic behavior has been reached.

As stated by Harvey *et al.*¹⁷ when dealing with experimental data the K_D^0 factor Eq. (7), gives a better estimate of the true asymptotic slope and a good agreement with the a_{Vx}^c from experimental critical-line data whereas the slope from the Henry's constant, Eq. (6), does not.

It is a fact that the hydration and dissociation of CO₂ in water cannot be separated from its dissolution. In this treatment the total CO₂ dissolved is considered, regardless of the species present in solution. This assumption can be made because any species other than $CO_2(aq)$ [the not yet isolated, so-called "carbonic acid" $\left(H_2CO_3\right)_{aq},$ the $H^+,$ and the HCO_3^{-}] in a solution of CO_2 in water exist in negligible amounts. These species can be ignored because the ratio of the molalities of $(H_2CO_3)_{aq}$ to CO_2 is about 3/1000 at 298.15 K (Ellis¹⁸). Also, experimental and theoretical arguments of Kruse and Franck¹⁹ indicate that $(H_2CO_3)_{aq}$ is not an important species at higher temperatures. The acidity constant of CO_2 goes through a maximum value of 6.3 10^{-1} mol kg⁻¹ at 353 K and decreases at higher temperature,^{20,21} so that the quantity of ionic species should become smaller as the temperature increases beyond 353 K. Whenever necessary, values for pure water properties such as ρ , f_{1}^{*} , and P_{1}^{*} were taken from Haar et al.22

2.1. Temperature dependence of kº

Any formulation that attempts to cover the entire liquid range of the solvent should be consistent with the facts that the derivative $(d \ln k^0/dT)_s$ diverges to $-\infty$ as $T - T_c$,¹⁶ that the infinite dilution solute partial molar isobaric heat capacity of dissolution in the saturated liquid, C_{p2}^0 , diverges to $+\infty$ as $T - T_c$, and that the value of k^0 at T_c is a constant equal to P_1^* times ϕ_2^0 .

Several empirical equations for the dependence of k^{0} on T are in common use: Clark and Glew,²³ Valentiner,²⁴ Benson and Krause,²⁵ and Fernández Prini and Crovetto.²⁶ These representations perform well in narrow temperature intervals and are not recommended for extrapolation outside the temperature interval used in the fit.

The simplest equation that can represent within the estimated overall experimental uncertainty the complete lowtemperature data set, was selected:

$$\ln(k^{0}/\text{bar}) = A_{0} + A_{1}(T)^{-1} + A_{2}(T)^{-2}$$
. (8) or P3

The three-term polynomial, Eq. (8) will be labeled as P3. P3 obviously does not fulfill the thermodynamics conditions at the critical point of the solvent.

For the high-temperature data set other equations were

used. An empirical equation proposed by Alvarez *et al.*,¹⁰ and by Fernández Prini and Crovetto,²⁷ that considers at least qualitatively some of the limiting features of k^0 , is

$$\ln(k^{0}/\text{bar}) = b(T_{c} - T)(T)^{-1} \ln[(T_{c} - T)/T_{c}] + A_{0} + A_{1}(T)^{-1} + A_{2}(T)^{-2}.$$
(9) or P3 + b

where b is considered as a free parameter.¹⁰ Equation (9), a three-term-polynomial plus a term leading to a diverging critical slope, will be labeled P3 + b. It does not predict the correct exponent of the temperature dependence and cannot be used for extrapolation beyond the fitted temperature interval in which data are available.

Recently, Krause and Benson²⁸ presented a new threeparameter equation in fractional powers of the temperature for representing solubilities at high temperatures. This equation will be labeled KB3. The equation does have the correct temperature dependence at the critical point.

Harvey and Levelt Sengers²⁹ correlated experimental data for solubilities of several gases in water and other solvents with a three-term expression. Asymptotically, near the critical point, the dominant term is linear in the density of the solvent, as in Eq. (6).

Their philosophy is followed here in the develop of a new equation for aqueous CO_2 . To obtain the correct limiting behavior as $T \rightarrow T_c$, the parameter of the term that would lead to the critical behavior is set equal to *B*. The coefficient *B*, Eqs. (6) and (7), can be obtained from fitting equation KD to infinite dilution distribution coefficient data, or from reliable experimental critical-line slopes, if available.

The proposed equation is

$$T \ln(k^{0}/f_{1}^{*}) = A' + B(\rho_{1}^{\text{liq}^{*}} - \rho_{c1}) + B_{1}(\rho_{1}^{\text{liq}^{*}} - \rho_{c1})^{2} + CT\rho_{1}^{\text{liq}^{*}} \exp[(273.15 - T)/50]. (10) \text{ or DEN*2}$$

Equation (10), a three-parameter equation with quadratic dependence on the pure solvent density, will be referred by means of the label DEN*2. In order to have an explicit formulation in terms of the temperature only, which would be easier to use for calculation purposes, Eq. (10) is reformulated. In order to change from the variable ρ to the variable T the asymptotic $\rho - T$ coexistence curve relationship combined with results of scaling laws for pure water was used. (See Levelt Sengers *et al.*³⁰) Thus, from the asymptotic relationship:

$$(\rho_1^{\text{liq}^*} - \rho_{c1})/\rho_{c1} = 2.105 [(T_c - T)/T_c]^{1/3},$$
 (11)

 ρ as a function of T can be obtained. For simplicity, in Eq. (11), the true nonclassical exponent $\beta = 0.326$ has been rounded to 1/3 and the critical amplitude from Ref. 30 has been slightly modified to counteract this change.

The fugacity of pure water in Eq. (10) can be expressed as a polynomial in inverse powers of T. Incorporating these two changes in Eq. (10) the simple three-parameter expression is obtained:

$$\ln(k^{0}/\text{bar}) = B_{T}(1 - T^{\#})^{1/3}(T)^{-1} + A_{0}$$
$$+ A_{1}(T)^{-1} + A_{2}(T)^{-2},$$
(12) or T*(1/3)

to represent the solubility, where $T^{\#} = T/T_c$. Note that the first term on the right is the term leading to the asymptotic critical behavior and is not adjustable. It equals

$$B_T = 2.105 \rho_{c1} B$$
,

with parameter *B* obtained, as stated before, either from experimental distribution coefficients, KD equation, or from critical-line slopes. Equation (12) is labeled $T^*(1/3)$.

The equations KD, DEN*2, T*(1/3), and KB3 are all consistent with the thermodynamic limiting requirements for $T \rightarrow T_{c1}$.

3. Solubility of CO₂ in Water

3.1. Literature Reviewed

All sources have been consulted that are cited from 1907 to 1989 in the Chemical Abstracts, the International Critical Tables, and Landolt Bornstein's Zahlenwerten und Funktionen (Volumes on Equilibrium).

The actual references used are presented in Table 1. The experimental data have been retrieved from these references and converted to a standard system of units of concentration, mole fraction of dissolved gas, x, total pressure, P, and temperature, T. In this way it is possible to conduct the thermodynamic treatment for all the sources on the same basis.

Sources that were not considered were those where only graphical results were presented or, in the case of the high-temperature data set, those from which the raw experimental data P,T,x could not be retrieved.

For the system CO_2 -H₂O a wide range of temperature and pressure conditions were covered by numerous sources. In different ranges, the assumptions and approximations required to extract Henry's constants from the data, vary considerably. Also, the precision of the low-temperature measurements is usually larger than that of the high-temperature data set. The data sources were therefore separated into three groups, to be treated separately.

Group A: solubility measurements from 273 to 353 K, P < 2 bar.

Group B: solubility measurements from 273 to 353 K, P > 2 bar.

Group C: solubility measurements from 353 K up to the critical temperature of the solvent and at any pressure.

Because of this arbitrary division, some sources fit into more than one group. In those cases the data were partitioned between the groups in accordance with the range of pressures and temperatures.

3.1.a. Group A, Low Temperature, Low Pressure

This group has the largest number of original sources, namely 24, with a total of 235 data points. The solubility of CO_2 in H_2O at low temperatures, though thoroughly researched, lacks both the precision and agreement among different methods of measurements that have been achieved for other systems of inert gases in water at low temperatures. (For example, see O_2 -H₂O, Benson *et al.*²⁵)

Unfortunately, although the number of sources of solubility data at low temperatures is relatively large they do not TABLE 1. Sources of data.

Group A (2	773 < T < 353 K, $P < 2$ bar)	Group B (le This group	by temperature, $273 < T < 353$ K, $P > 2$ bar) was not considered in the formulation.
AUS(63):	Austin, W. H.; Lacombe, E.; Rand, P. W.; Chatterjee, M., J.	KRI(35):	Kritschewsky, I. R.; Shaworonkoff, N. M.; Aepelbaum, V.
BO(891):	Appl. Physiol. 1905, 18, 301–304. (3:5) Bohr, C.; Bock, J., Ann. Phys. Chemie, NF 1891, 44, 318– 343. (2:0)	MAT(69)-	A., Zeit. Phys. Chem. A 1935, 175, 232–238. <i>i</i> , <i>P</i> : 5–30 bar, (2:0). Matuma L: Subr. L: Novak, L.P.: Pick, L. Coll. Czech
BO(899): BU(855):	Bohr, C., Ann. Phys. Chemie 1899, 68 , 500–525. (15:15) Bunsen, R. W. E., Philos. Mag. 1855, 9 , 116–130, 181–201;		Chem. Comm. 1969, 34 , 3982–3985. <i>ii</i> , <i>P</i> : 9–35 bar, (3:0).
	Gasometrische Methoden, Braunschweig 1857. The same experimental points are also published in: Bunsen, R. W. E.,	SHA(82):	Shaiachmetou, R. A.; Tarzimanov, A. A., Dep. Doc. 1981. SPSTL 200-khp-D81, 1982. <i>ii</i> , <i>P</i> : 100-400 bar, (1:0).
DUCION	Justus Liebig's Annalen der Chemie (also Ann. Chem.) 1855, 93 , 1–50. (6:5)	STE(70):	Stewart, P. B.; Munjal, P., J. Chem. Eng. Data 1970, 15, $67-71. ii, P_2 \approx 10,40$ bar, (12:0).
BUC(28):	Buch, K., Nord, Kemiskmotet (Finland) 1928, 184–192. (14:7)	VIL(67):	Vilcu, R.; Gainar, I., Rev. Roum. Chim. 1967, 12 (2), 181– 189. <i>ii</i> , $P_2 \approx 25,70$ bar, (20:0).
CRA(82):	Cramer, S. D., Bureau of Mines Report of Investigations 1982, RI 8706. (1:0)	WIE(30):	Wiebe, R.; Gaddy, V. L., J. Am. Chem. Soc. 1939, 61 , 315–318. <i>i</i> , <i>P</i> : 25–700 bar, (2:0).
CUR(38):	Curry, J.; Hazelton, C. L., J. Am. Chem. Soc. 1938, 60, 2771-3. (4:2)	WIE(40):	Wiebe, R.; Gaddy, V. L., J. Am. Chem. Soc. 1940, 62, 815–817. <i>i</i> . <i>P</i> : 25–500 bar, (5:0).
HAR(43):	Harned, H. S.; Davies, R., Jr., J. Am. Chem. Soc. 1943, 65, 2030–2037. (18:18)	ZAW(81):	Zawisza, A.; Molesinska, B., J. Chem. Eng. Data 1981, 26 , 388–391. <i>ii</i> , $P_2 \approx 25$ bar, (9:0).
KH(807):	et de Physique (Quatrieme Serie) 1867, 11, 412-433 (10-1)	Group C (7	7>373 K, any P)
KOB(35):	Kobe, K. A.; Williams, J. S., Ind. Eng. Chem. (Am. Edition) 1935. 7(1). 37–38. (1:1)	BO(891):	Bohr, C.; Bock, J., Annalen der Physik und Chemie, NF 1891 44 318-343 <i>ii</i> 373 K (1-0)
KOC(49):	Koch, H. A., Jr.; Stutzman, L. F.; Blum, H. A.; Hutchings, L. E., Chem. Eng. Progress 1949, 45 (11),	CRA(82):	Cramer, S. D., Bureau of Mines Report of Investigations 1982, RI. <i>ii</i> , 399–486 K, (6:2).
101 101 (00)	677–682. (6:1)	CRO(90):	Crovetto, R., Wood, R. H., Fluid Phase Equilibria, to be
KUN(22): LI(71):	Kunerth, W., Phys. Rev. 1922, 2, 512–524. (8:6) Li, Y. H.; Tsui, T. F., J. Geophys. Res. 1971, 76 (18), 4203– 4208. (5:5)	ELL(63):	submitted. <i>ii</i> , <i>i</i> , <i>P</i> : 170–220 bar, 623–640 K, (3:3). Ellis, A. J.; Golding, R. M., Am. J. Sci. 1963, 261 , 47–60. <i>ii</i> , 450–607 K (15:14)
MAR(41):	Markham, A.; Kobe, K., J. Am. Chem. Soc. 1941, 63 , 449– 454. (3:3)	MAL(59):	Malinin, S. D., Geokhimia 1959, 3 , 235–45. <i>i</i> , <i>P</i> :100–500 bar, 473–603 K. (4-2)
MOR(30):	Morgan, J. L. R.; Pyne, H. R., J. Phys. Chem. 1930, 34, 1578–81 (2:0)	SHA(82):	Shaiachmetou, R. A.; Tarzimanov, A. A., Dep. Doc. 1981, SPSTL 200 kph D81, 1982. <i>A</i> , P. 100-800 bar, 373-423
MOR(31):	Morgan, O. M.; Maass, O., Can. J. Res. 1931, 5 , 162–199. (19:4)	TAK(65):	K, (2:2). Takenouchi, S.; Kennedy, G. Am. J. Sci. 1965, 263 , 445–454.
MOR(52):	Morrison, T. J.; Billet, F., J. Chem. Soc. 1952, 3819– 3822. (19:19)	WIE(39):	<i>i</i> , <i>P</i> : 200–1400 bar, 423–623 K, (5:4). Wiebe, R.; Gaddy, V. L., J. Am. Chem. Soc. 1939, 61 ,
MUR(71):	Murray, C. N.; Riley, J. P., Deep-Sea Res. 1971, 18, 533–	7.4 15/(01)	315–318. <i>i</i> , <i>P</i> : 25–700 bar, 373 K, (1:1).
NOV(61):	Novak, J.; Fried, V.; Pick, J., Collect. Czech. Chem. Com- mun. 1961, 26 , 2266–2270. Measurements at different pres- sures at 8 different constant <i>T</i> . From the slope of k vs x , k^{0} is	ZAW(81):	Zawisza, A.; Molesinska, B., J. Chem. Eng. Data 1981, 26, 388–391. <i>ii</i> , 373–473 K, (24:24).
ORC(36):	calculated. (8:0)" Orcutt, F. S.; Seevers, M. H., J. Biol. Chem. 1936, 117 , 501-507 (1:1)	The me For gro	aning of the symbols used in the table is as follows: up A: the numbers in parentheses, (m,n) , are: m the number of points given in the source or do the symbol n is interval.
POW (70):	Power, G. G.; Stegall, H., J. Appl. Physiology, 1970, 29, 145–9 (1-1)	considered i	r points given in the source, and n the number of points actually in the evaluation.
PR(895):	Prytz, K.; Holst, H., Ann. Phys. Chemie, NF 1895, 54 , 130– 138. (2:0)	available for for Henry's	\dot{c} different pressures. When feasible, a graphical extrapolation constant k to solvent variance pressures was parformed. The
SHE(35):	Shedlovsky, T.; MacInnes, D. A., J. Am. Chem. Soc. 1935, 57, 1705–10. (1:1)	numbers in p	parentheses, $(m;n)$, are: m is the number of k^{os} obtainable from i is the number actually considered ii only one pressure or a
VAN(39):	Van Slyke, D. D., J. Biol. Chem. 1939, 130 , 545–554. (6:6)	very small p number in p	ressure range, was experimentally studied in the source. The arentheses, $(m;u)$, arc; m in this case is the number of experi-
VE(855):	Verdet, M.; report of Bunsen's, M., Ann. Chim. Phys. 1855, 43, 496–508. (21:0) [#]	mental point tion. The exp	s informed, <i>u</i> is the number of points considered in the evalua- perimental partial molar volume of the solute is considered for
YEH(64):	Yeh, S. Y.; Peterson, R. E., J. Pharm. Sci. 1964, 53, 882- 874. (4.3)	calculating k	e^{0} in Eq. (1). B C the range of P and T of the measurements are since in
#See text for	detail about source rejection.	group B, onl	$p \in (n \in range of P)$ and P of the measurements are given, in by the range of P.

overlap over a temperature interval big enough to provide an unquestionable statistical description of the temperature dependence of the solubility.

In this group eleven different ways of expressing the solubility or the concentration of CO_2 in water were found. The alphabetical listing of the sources in this group is given

in Table 1 together with information on the number of data points in each source and the number of data actually considered in our formulation. Details of the approximations involved in the calculation of k^0 from Eq. (1) for this group are presented in Appendix I.1.a.

All the available sources and a standard procedure of

TABLE 2. Adjusted coefficients for the equations P3, P3 + b, KD, DEN*2, T*(1/3). The last four ones, have been fitted to values of k^{0} calculated from PR and W EOS. [Coefficients informed for P3, P3 + b, T*(1/3) are for k^{0} in bar.] The last column, $\%\sigma$, is the % standard deviation of the fit for k^{0} values.

Equation	A ₀	A_1/K		A_2/\mathbf{K}^2	%σ
<u>P3</u>	4.800	3934.40		- 941 290.2	1.1
P 3 + b	Ь	A ₀	<i>A</i> ₁ /K	A_2/K^2	
EOS:PR	- 3.608	4.610	2849.08	- 833 050.2	3.9
:W	- 3.341	4.515	2999.98	- 852 374.3	4.1
KD		2 <i>B</i>	coef.sd.dev		
		K.(mol/liter)	- 1		
EOS:PR		91.22	0.18		8.6
:W		90.55	0.20		9.5
DEN*2	A'		<u> </u>	С	
	K		$K(\text{mol/liter})^{-2}$	(mol/liter) ⁻¹	
EOS:PR	994.85		0.5129	- 0.0174	5.2
:W	1033.29		0.4786	- 0.0165	5.2
B fixed to $45.54 K (mol/liter)^{-1}$	' in both.				
T*(1/3)	Ao		A./K	A_2/K^2	
EOS:PR	3.875		3680.09	- 119 850 6.1	5.0
:W	3.584		3886.17	123 422 7.6	5.3
low + high $T(PR)$	3.982		3555.40	- 116 989 9.3	3.8
B_T fixed to 1713.53 K for all. $T_c = 647.126$ K, $\rho_c = 17.874$ n	nol/liter.				

point rejection (see Appendix II) have been used. After studying the resulting preliminary nonrejected data deviation plot I have discarded those sources that, although on average in agreement with other data, contribute large scatter. Specifically these were the data by Novak, NOV(61), and Verdet, VE(855).

For the remaining data equation P3 was used as the fitting equation. The optimized coefficients of the unweighted fit and the standard deviation of the fit are given in Table 2. P3 is to be used from 273 to 353 K. No extrapolation beyond the temperature interval is recommended.

The data measured by Weiss,⁷ which were included in the review of Wilhelm *et al.*,⁴ have not been considered here because the original raw data cannot be retrieved from the published k^0 values.

The major differences between this review and Wilhelm $et al.^4$ are: the number of sources considered, the data treatment, and the fitting equation used.

Wilhelm *et al.* took into account only three sources: Morrison and Billet,⁵ Murray and Riley,⁶ and Weiss.⁷ In this evaluation instead twenty four original sources that, after the rejection criteria, resulted in nineteen sources are considered. Weiss⁷ measured solubility only at about 20.6 °C and had corrected his data for the nonideality of CO₂ and for ionization. Weiss also corrected and recalculated the data of Murray and Riley⁶ and fitted them to an equation. It is these recalculated values that were used by Wilhelm *et al.*,⁴ instead of the original ones. Wilhelm *et al.* also used only eight of the nineteen original Morrison and Billet⁵ data points. For expressing their results they used a 4-parameter Clarke and Glew²³ type of equation, obtaining a percent standard deviation, σ %, of 0.54 for the fit.

Calculated Henry's constant from the same original sources used by Wilhelm *et al.*, were fitted with a 3-parameter equation, P3. The percent standard deviation, σ %, of the fit is 0.57, which is only marginally larger than that of Wilhelm *et al.* Adding more terms to P3 is not statistically significant.

Table 3 presents smoothed values of $\ln k^{0}$ calculated from P3, at selected temperatures. Values of $\ln k^{0}$ are tabulated for: all the nineteen sources considered, only Morrison and Billet⁵ and Murray and Riley⁶ adjusted to a P3 equation, and the corresponding values calculated from the equation of Wilhelm⁴ et al.

As can be seen from the Table 3, there is almost no difference between $\ln k^0$ values obtained with P3 fitted to all the sources, as compared to P3 fitted to only two sources. There is, however, a difference with Wilhelm *et al.*'s values that increases with temperature. The divergence is as much as 2% lower than our prediction at the highest temperature of the fitting interval, 353 K, and represents three and one-

TABLE 3. Values for ln k° calculated at different temperatures, from Eq. P3, for all the sources P3(all); for the two sources Morrison and Billet⁵ and Murray and Riley,⁶ P3(2); and from the equation of Wilhelm *et al.*⁴

		$\ln(k^0/\text{bar})$	
T/K	P3(all)	P3(2)	Ref. 4
273.15	6.588	6.594	6.600
283.15	6.955	6.958	6.962
293.15	7.268	7.270	7.274
303.15	7.536	7.537	7.542
313.15	7.765	7.766	7.771
323.15	7.961	7.962	7.964
333.15	8.129	8.130	8.127
343.15	8.272	8.274	8.262
353.15	8.393	8.397	8.372

half times the standard deviation of any of the individual fitting equations.

These differences between the results from the lowest and the highest temperature of the interval, 273 and 353 K in this case, is a well-known problem when empirical equations are used. The origin if the different curvatures in the equations used to represent Henry's constant as a function of temperature. The difference in number of sources considered or the data treatment cannot be the cause as the result of fitting to P3 the same sources as Wilhelm *et al.* shows (third column in Table 3).

In contrast to Wilhelm *et al.*, I have used data obtained by several different experimental methods, with about the same estimated precision and reproducibility. Systematic errors characteristic of one particular experimental technique have less of an opportunity to bias the fitting equation if data from many different origins are fitted simultaneously.

Equation P3 is chosen to fit all the data sources (Table



FIG. 1. Deviation plot, as $[\ln(k^0/bar)_{exp} - \ln(k^0/bar)_{calc}]$ versus temperature for Group A, Eq. (3), P3 (a) with Novak *et al.*, NOV(61), and Verdet *et al.*, VE(855) and (b) without them. (c) Only two sources considered. Symbols are as follows: $\pm 15HE(35)$, \bigcirc POW (70), \triangle AUS(63), \pm CUR(38), \times MOR(30), \Diamond NOV(61), \bigtriangledown KUN(22), $\exists \pm YEH(64)$, $\exists \in MOR(52)$, $\oint MAR(44)$, $\pm HAR(43)$, \blacksquare VAN(39), \blacksquare ORC(66), \otimes KOB(35), \blacksquare KOC(49), \square MOR(31), \triangle MUR(71), $\Diamond \pm 11(7i)$, \lor BU(855), \blacksquare BO(899), $\pm 1PR(895)$, \clubsuit KH(867), \Diamond VE(855), \blacksquare BUC(28).



3, column 2) and to generate smoothed solubility data for anchoring the low-temperature end of the high-temperature formulation. In Table 4 the recommended values of k^0 for the low temperature data set are given.

A deviation plot of the fit for P3 vs temperature is given in Figs. 1(a), before discarding Novak *et al.*, NOV(61), and Verdet *et al.*, VER(855) and after discarding them, Fig. 1(b). In Fig. 1(c) a deviation plot for P3 fitted solely to the data sets of Morrison and Billet⁵ and Murray and Riley⁶ is shown.

From the plots it can be seen that sources above 323 up to 353 K are scarce, namely only one. To reduce the scatter further, more precise measurements are necessary, especially from 273 to 313 K. The deviation plot for all the sources does not show any particular systematic deviation or any nonstatistical behavior. The deviation plot of Fig. 1 when only two sources are considered, using equation P3, shows a feature characteristic of solubility measurements from different sources: Even with the same precision, one source is systematically below the other, although in this particular case, however, the differences do not exceed the precision of each source.

3.2. Group B, Low Temperature, Higher Pressure

This group consists of eight different sources, and is listed alphabetically in Table 1. From the experimental data, 23 values of Henry's constant were calculated at different temperatures. This group is very difficult to evaluate because for some experimental P and T conditions carbon dioxide is very near its critical point. This group has not been included in the formulation.

3.3. Group C, High Temperature, Any Pressure

There are nine different sources in this group that, after the proper analysis of the pressure dependence, results in 61 calculated values of k^0 at different temperatures. The sources are listed in Table 1. There are several other publications that deal with CO₂ solubility in various salt solutions, such as those of Onda *et al.*,³¹ and Malinin and Savaleyva,³² among others. The characteristic of these sources is that the measurement of the solubility of CO_2 in water is used as a test of the experimental procedure and is not a goal by itself. Those kind of sources are not considered in this evaluation.

Drummond's³³ Ph.D. dissertation has not been considered because he only gives the derived Henry's constant values and not the raw experimental data set. The values of P, T, and x cannot be retrieved from the source in order to treat them in the same way as for the other sources.

Drummond derived Henry's constant from an experimental procedure that is based on a mass balance, at constant volume, for the solvent and solute present in both phases. He does not consider the water-gas interaction in the vapor phase, even though it is known that this interaction is significant, especially above the vapor pressure of the solvent. (See Crovetto *et al.*³⁴)

Henry's constant for Group C have been calculated using four different EOS for the vapor mixture. Details are given in Appendix I.1.b.

This group was fitted to equations P3 + b, KD, DEN*2, and T*(1/3). Five low-temperature points, calculated from the low-temperature equation P3 (as described in Sec. 3.1), were added at 273.15, 293.15, 303.15, 323.15, and 353.15 K in order to complete and anchor the data set for fitting. This was done for all the equations *except* for KD. It is not expected that the equation KD will be valid for low temperatures. (See Japas and Levelt Sengers.¹⁶)

All the solubilities considered were given the same weight in the fitting procedure.

In this particular system the linear relationship of equation KD is observed starting at densities corresponding to about 373 K. For CO_2 -H₂O system the slope of the KD equation (2B) is observed to vary very little, about 0.1% whether the highest temperature data points, Crovetto and Wood, CRO(90), were considered or not.

Although its asymptotic critical behavior is not correct equation P3 + b is included because it is the one giving the

TABLE 4. Recommended values for k^{0} calculated from the selected fitting Eq. P3, considering all the sources, at 5 K intervals from 273.15 to 353.15 K (σ standard deviation of the fit.)

T/K	k ⁰ /bar	$\pm \sigma/bar$
273.15	726	8
278.15	879	10
283.15	1048	12
288.15	1233	14
293.15	1433	16
298.15	1648	18
303.15	1874	21
308.15	2111	23
313.15	2357	26
318.15	2610	29
323.15	2868	32
328.15	3128	34
333.15	3391	37
338.15	3652	40
343.15	3912	43
348.15	4167	46
353.15	4418	49

TABLE 5. Values of $\ln(k^0/\text{bar})$ obtained by means of different EOS, PR, and W, and smoothed by the Eq. DEN*2, T*(1/3) and KD.

			$\ln(k^0/\text{bar})$		_
	DE	N*2	T*(1/3)	K	D
T/\mathbf{K}	PR	w	PR	PR	W
353.15	8.412	8.405	8.415		
368.15	8.534	8.528	8.544		
383.15	8.612	8.613	8.632	8.674	8.660
398.15	8.669	8.669	8.687	8.694	8.683
413.15	8.696	8.699	8.715	8.695	8.689
428.15	8.703	8.709	8.721	8.683	8.682
443.15	8.692	8.701	8.708	8.658	8.662
458.15	8.666	8.679	8.679	8.623	8.633
473.15	8.627	8.643	8.636	8.579	8.594
488.15	8.577	8.596	8.582	8.526	8.547
503.15	8.515	8.538	8.518	8.465	8.492
518.15	8.443	8.470	8.445	8.397	8.431
533.15	8.361	8.391	8.363	8.322	8.363
548.15	8.268	8.302	8.271	8.239	8.288
563.15	8.163	8.200	8.171	8.149	8.207
578.15	8.043	8.083	8.060	8.050	8.118
593.15	7.905	7.949	7.935	7.940	8.020
608.15	7.741	7.788	7.790	7.798	7.911
623.15	7.531	7.582	7.611	7.632	7.783
638.15	7.216	7.271	7.344	7.381	7.514
643.15	7.037	7.094	7.187	7.231	7.215
647.10	6.601	6.661	6.791	6.675	6.414

T.: 647.126 K

smallest standard deviation. P3 + b should not be used to extrapolate outside the temperature interval considered to adjust its coefficients, 273–642 K.

Benson and Krause's²⁸ three-parameter equation, KB3, has been tried to fit the values of $\ln k^0$ vs *T*. The standard deviation of the corresponding fit is about 16%. This is not considered a satisfactory representation for this system and therefore, the corresponding coefficients are not given.

The adjusted parameters for equations P3 + b, KD, DEN*2, T*(1/3) obtained by using different EOS for calculating the vapor phase nonideality are presented in Table 2 together with the % standard deviation, $\sigma\%$, for k^0 . For details on the EOS see Appendix I.1. Smoothed values for Henry's constant from KD, DEN*2 for W and PR EOS and

T*(1/3) for W, at intervals of 15 K from 353 to 647.1 K are given in Table 5. Table 5 illustrates differences observed in $\ln k^0$ for different fitting equations and EOS. For a given equation, the variation in k^0 above 500 K due to the use of two different EOS (marked PR and W) for the vapor phase amounts to several percent (Table 5, compare columns 2 with 3 and 5 with 6). Also, for different fitting equations and the same EOS for the vapor phase, the variation in k^0 is inside the fitting uncertainty but above 608 K becomes very large (Table 5, compare columns 2, 4, and 5).

The standard deviation of this fit is about three times that obtained at low temperatures.

As no qualitative differences are observed in the residual distribution versus temperature for the equations used in the fit of Group C, only deviation plots as a function of the temperature for KD and $T^*(1/3)$ using both PR and W EOS are presented in Figs. 2(a) and 2(b), respectively.

The overall shape of the deviation plots is the same independent of the fitting equation and/or the EOS used. The conclusion is then that the pattern must probably be due to systematic differences among data sets.

All fits seem to represent the data well but they do differ somewhat in the standard deviation found.

An attempt was made to represent all available experimental points at both low and high temperatures with $T^*(1/3)$.

For the calculation of the high-temperature k^0 , the PR EOS was used.

 $T^*(1/3)$ is selected because it already has terms of the same mathematical type, three terms in inverse of power of temperature, as the expression used to fit the low-temperature solubility P3. No weighting procedure was used.

The percent standard deviation obtainable is 3.8, whereas the one for high temperature is 5.0 and for the low temperature is 1.1. However as the precision and the number of points in each temperature region are so different, the representation is definitely biased by the greater number of experimental points in the low-temperature region. Many of the high-temperature points have in this representation a residual that is two or three times the standard deviation of the fit. The adjusted coefficients are given in Table 2.

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□ ELL(63), △ WIE(39), + CRA(82), × ZAW(81), [◊] SHA(82),
 ▼ TAK(65), ■ MAL(59), × CRO(90), [◆] low T data from eq.(5).





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4. Conclusions

From the evaluation of the existing solubility data for this system it can be concluded that more precise measurements, of the quality of those of Benson *et al.*,²⁵ are needed in the low-temperature region, 273 < T < 353 K, if a precision similar to that of other gases in water is desired.

For the high-temperature range there is a need for more precise, reproducible measurements, especially near the minimum of the solubility (at about 400 K), and also for the range above 500 K. As results of this evaluation show, however, in order to obtain reliable values for k⁰ above 500 K one needs not only more exact and precise measurements, but in addition to have a reliable EOS for the vapor phase of the CO₂-water system that could give the correct fugacity coefficients for the solute in the vapor phase. As can be seen in Table 5, above 500 K, the use of different and reasonable guesses of EOS for the vapor phase produces an uncertainty which slowly increases with the temperature and that can be as high as 8% in k^0 at 643 K. Also, the use of different representative equations, with k^{0} values calculated from the same EOS, predict slightly different values, with 1%-5% uncertainty in k^{0} up to 608 K. The difference in predictions increases greatly from 608 K and upwards being as large as 20% at 647.1 K.

Combining all of these factors, for the Henry's constant values, k^0 , for this system between 273 and 353 K, an uncertainty of 1% is estimated; and between 353 and 600 K an uncertainty of about 5%–10%. For temperatures above 600 K the uncertainty increases very quickly to at least 20% near the critical point of water.

For calculating a low temperature, 273 to 353 K, Henry's constant P3 is recommended, which was fitted to all the sources. The corresponding coefficients are reported in Table 2. The equation is reproduced here together with the corresponding $\%\sigma$, in k^0 , of the fit.

$$\ln(k^{0}/\text{bar}) = 4.800 + 3934.40(T/K)^{-1}$$
$$-941\ 290.2(T/K)^{-2}, \quad \%\sigma = 1.1.$$

For calculating Henry's constant above 353 K, $T^*(1/3)$ is recommended, fitted to Henry's constants obtained with the use of the Peng and Robinson equation of state. Although the corresponding coefficients are listed in Table 2, the equation and the percent standard deviation in k° are repeated here.

$$\ln(k^{0}/\text{bar}) = 1713.53(1 - T^{\#})^{1/3}(T/K)^{-1}$$

+ 3.875 + 3680.09(T/K)^{-1} - 119 850 6.1
× (T/K)^{-2}, %\sigma = 5.0

where $T^{\#} = T/T_c$.

The recommendation is based on the fact that it is not only a very simple equation to use, but is the equation that gives the smallest rms deviation when k^0 values are compared with predictions of k^0 calculated from the KD equation, with coefficients adjusted for PR EOS, and combined with Eq. (5). With this statement it is implicitly assumed that equation KD can give the most reliable estimates for the solubility, especially at high temperatures. Equation DEN*2 is also suitable, but requires input of densities and fugacity coefficients for pure water.

The ultimate goal of a representation of all data, both at low and high temperatures, within the precision of the individual measurements, with only one equation could not be attained.

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Appendix I. Procedure for calculation of Henry's constant

In this appendix the procedures and the assumptions used to calculate k^0 according to Eqs. (1) and (2) are described. Every source of data was reduced to the same information, i.e., temperature, total pressure, and molar fraction of carbon dioxide dissolved in the liquid. Thus all the data received the same thermodynamic treatment.

I.1. Equation of State

In different temperature regions, different assumptions are made. They are discussed separately below.

I.1.a. Low-temperature solubility data (Group A)

For definition of units of solubility and their relation, see reviews in Clever and Battino³⁵ or Wilhelm and Battino.³⁶ To convert Bunsen's and Kuenen's coefficients to mole fraction the real volume of CO₂ at normal pressure and temperature was used (24.340 l/mol). Since solubilities expressed as Ostwald's coefficient were found only for T < 320 K and P < 1.5 bar, the following assumptions were used to calculate the mole fraction: Molar volume of the solution equals molar volume of water at the same temperature, a second virial coefficient EOS for the gas phase considered to be pure CO₂. (The water content in the vapor phase at these conditions is very small.)

To calculate the solubility, the vapor phase of group A can be described by means of a mixture second virial coefficient EOS. The cross virial coefficients as a function of temperature were taken from Dymond and Smith's compilation.³⁷

The procedure to obtain y and ϕ_2 needed in Eq. (1) is iterative and is described in detail elsewhere, Crovetto *et al.*¹⁴ When comparing our results for the low temperature data with those of Wilhelm's *et al.*,⁴ in Table 3, columns 2 and 4, it has to be pointed out that the data they used for low temperature solubilities (Weiss⁷ and Murray and Riley⁶), had been corrected for nonideality, but that the data they used for the highest temperatures, Morrison and Billet,⁵ had not. At the highest temperature, however, the nonideality correction can only account for about $\mp 0.5\%$ in k^0 , whereas the observed differences, Table 3, accounts for 2% at the end of the temperature interval. As discussed in the text, this is mainly due to the different functionality with the temperature, curvature, in the equations used to calculate k^0 and not to nonideality corrections.

I.1.b. High temperature data (Group C)

The selection of a reasonably good and simple EOS that could describe CO2-H2O in the vapor phase was not an easy task. A good EOS should not only predict accurate volumetric quantities and P, T, x, y for phase separation, but also that yield accurate derivatives for the pressure with respect to the number of moles, or fugacity coefficients. These conditions are not necessarily simultaneously true for a given EOS. For the system CO₂-H₂O there are several options. The influence of the selected EOS on the value of k^0 , especially near the critical point of water is tested. Since no analytical equation will be exact for the critical region, one must expect that corrections are most uncertain in this region. The selected EOS will determine the equilibrium vapor composition y and the fugacity coefficient ϕ_2 to be used in Eq. (1) for calculating k^0 . What really matters in Eq. (1) is the product of y and ϕ_2 . Individual variations of y and ϕ_2 can compensate, be larger or smaller, or have different pressure dependence, depending on the EOS used in the calculation.

A natural fundamental EOS for intermediate and low densities away from the critical density, is the virial EOS, V_1 , an expression for the pressure along isotherms in powers of the density of the fluid mixture.

The mixture second virial cross coefficient, $B_{1,9}$, for CO_2 -H₂O were measured by Coan and King³⁰ up to 373 K, and more recently by Patel *et al.*³⁰ and by Wormald *et al.*⁴⁰ up to 498 K. B_{12} values from different sources are in very good agreement. There is also an estimation of B_{12} values for this system up to 1100 K from Vanderzee *et al.*⁴¹ Third virial cross coefficients C_{112} and C_{123} have been measured for this system up to 498 K, by Patel *et al.*⁴⁰ The temperature dependence of the third virial coefficients was extrapolated up to the critical point of water by making educated guesses about their possible values. (For instance, C_{122} was already almost constant at 498 K so its value at higher temperatures was taken as constant.)

City values are already starting to decrease at 498 K and

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above. To estimate its temperature dependence a value similar to that of the third virial coefficient for pure water vapor was assigned to it at 1200 K and C_{112} 's were fitted as a function of temperature. Second and third virial coefficients of pure water as functions of the temperature were obtained from the formulations in the NBS/NRS Steam Tables of Haar *et al.*²² Second and third virial coefficients of pure CO₂ were taken from Vukalovich and Altunin.⁴²

Peng and Robinson's¹¹ mixture EOS, PR, which is capable of adequately describing vapor-liquid equilibria in water-apolar gas systems, was another equation used. The equation has a mixture parameter, δ_{12} , that is independent of temperature and pressure, B_{12} , of the mixture. In disagreement with the general behavior observed for several other binary mixtures of apolar gases and water vapor, see Fernández Prini and Crovetto,²⁷ a pronounced temperature dependence of δ_{12} for temperatures below 373 K, if δ_{12} is obtained from the reported values of B_{12} is observed. Analyzing the actual dependence of δ_{12} on temperature, an average value of $\delta_{12} = 0.285 \pm 0.035$ is found to be approximately independent of temperature between 375 and 650 K. This value was used as the mixture parameter δ_{12} when the PR equation is used. The necessary pure components parameters for the PR equation were obtained from the literature, Reid et al.43

Gibbons and Laughton,¹² G, presented a simple cubic equation of state for polar and nonpolar substances and mixtures as a modification of the Redlich–Kwong–Soave equation. They fitted their mixture interaction parameter so as to represent the experimental liquid-vapor compositions of several mixtures, among them CO_2 –H₂O. Their mixture value of -0.06 was used in the calculations. Pure components parameters values were taken from the literature, Reid *et* $al.^{43}$ Recently, Wormald and Lancaster,¹³ W, presented a cubic EOS for gaseous mixtures containing steam. Their EOS, with their mixture rules, and the interaction parameter they obtained for the CO_2 -H₂O system are used.

From the four selected EOS y is calculated from Eq. (2) with an iterative procedure described elsewhere, Crovetto et al.,¹⁴ and then the corresponding ϕ_2 at that composition from the same EOS. With these values and the experimental measured quantities, k^0 can be obtained from Eq. (1) when the partial molar volume of the solute in the liquid, V_2 is known. (Regarding values of V_2 used, see Sec. I.2.)

When using Vi as EOS mathematical problems are found, such as imaginary roots for the volume of pure water at its vapor pressure at 580 K and higher, or imaginary roots for the volume of the mixture at low temperatures for different pressures. The pressure interval that does not have mathematical problems increases with temperature (for instance, it ranges from 0 to 45 bar at 285 K, and from 0 to 100 bar at 323 K). At high temperatures there is no real solution for the volume of the vapor phase mixture starting at 300 bar and up at 423 K and from 157 bar and up, at 573 K. This restricts the P,T conditions where k^0 values calculated from different EOS can be compared with the resulting k^0 calculated from the virial EOS. The original goal was to use the more fundamental virial EOS as a test for the others, at least not very near the critical point of the solvent.

The four EOS were compared in their ability to predict the compressibility factor, Z, and the fugacity coefficient of pure water, from 373.15 to 643.15 K. Values for comparisons with pure water were taken from Haar *et al.*²²

As can be seen from the following table, any EOS will predict reasonably good values for ϕ_1^* almost up to the critical point of water, though the predicted Z values are quite poor.

EOS:		1	И		R	G		W	
T/K	%	ΔZ	$\Delta \phi_1^*$	ΔZ	$\Delta \phi_1^*$	ΔZ	$\Delta \phi_1^*$	ΔZ	$\Delta \phi_1^*$
373.15		0.001	- 0.03	0.6	- 0.6	- 0.67	- 0.6	0.03	0.0
473.15		0.14	0.03	- 2.3	- 1.6	- 2.7	-2.0	0.03	- 0.05
573.15		10.	1.3	— 4 .	- 0.5	- 6.1	- 2.4	0.2	- 0.4
623.15				- 8.	0.5	- 13.2	- 2.3	- 0.7	- 1.5
633.15				- 10.	0.8	16.5	2.2	- 2.5	_ 2.2
643.15				— 15 .	1.0	- 23.2	-2.2	<i>—</i> 27.	- 3.7

Percent differences in Z and ϕ_1^* between values calculated from EOS and Steam Table values for water vapor at different temperatures.

(The percentage change is the Steam Table value minus the EOS value, divided by the Steam Table value.)

Another way of comparing EOS performance is to test their ability to reproduce values for the known mixture 2nd virial coefficients as a function of the temperature. In this case δ_{12} of the PR equation was fitted to reproduce B_{12} from 375 K up. It was found that G EOS does not reproduce B_{12} values, but W EOS does. Comparing the vapor phase composition predictions from the EOS with the available experimental data from Wiebe and Gaddy,⁴⁴ Zawisza *et al.*, ZAW (81), and Patel *et al.*,³⁹ all EOS used reproduce the data fairly well, although none exactly and no systematic trend in the predicted values can be distinguished. Comparing values of k^0 calculated by means of the EOS Vi with values of k^0 calculated by means of PR, G, and W EOS at the same temperature, the values show a spread less than $\pm 1.5\%$ up to about 500 K. The smallest differences between k^{0} 's values are those derived from Vi and PR. For higher temperatures and as long as the use of Vi is possible, k^0 values calculated from PR and Vi differ less than 1%-2%. Differences in k^0 for the highest temperature measured, 642 K, are about 4% when comparing PR and G. When comparing W and PR, the difference increases slowly with the temperature, becoming as high as 8% at 642 K.

A useful comparison to do is to calculate, at constant temperature, and at increasing pressure, Henry's constant, k, calculated from Eq. (1) setting V_2 equal to zero (no pressure correction) and using different EOS for the vapor phase. The results are that from PR and V_1 EOS similar k values are obtained, the differences being less than 1%. From G and W EOS the results are that they would predict a different and bigger pressure dependence for k than either V_i or PR EOS. Differences in k values calculated from G or W compared to PR can be as large as 5% and 20%, respectively, for pressures of about 300 bar. Once again, the pressure dependence of k is a combination of the functional dependence on V_2 shown in Eq. (1) but also of the EOS used for ϕ_2 and sometimes experimental artifacts, Fernández Prini and Crovetto.²⁶ For this reason it is not recommended to calculate partial molar volume of the solute from the slope of $\ln k$ vs pressure at high vapor pressure of the solvent.

Nevertheless, as already stated, the *extrapolated* values for k^0 obtained by means of the PR and W EOS do not differ more than the stated 1.5% until about 500 K, although the difference slowly increases with the temperature being about 8% at the highest T measured.

The G EOS does not correctly predict B_{12} for CO₂-H₂O. It seems to predict too great a pressure dependence for k. Since k^0 values calculated using PR and G do not differ greatly, especially at pressures near the vapor pressure of the solvent, G is not used any further and to illustrate differences in calculated values of k^0 due to the use of different EOS PR and W are selected.

The mixture parameter of the W EOS has been adjusted to reproduce the excess molar enthalpies of mixtures. This, however, does not guarantee that the equation represents vapor phase fugacity coefficients of the dilute mixture properly, or that it can predict vapor phase compositions accurately.

An advantage of this equation is that it has been fitted to mixture properties, and the same cannot be said of PR EOS for this system. There is no strong argument to prefer one EOS over the other, but small observations lead us to recommend the PR over the W EOS. PR predicts better fugacity coefficients for pure water for temperatures near T_c (see corresponding table on p. 35).

When K_D^0 is calculated using in Eq. (5) k^0 values from PR EOS, it is found that Eq. (7), KD, has a smaller standard deviation and a better linear regression than when W EOS is used.

I. 1.c. Group B

For this group the PR EOS would probably be the most suitable EOS for the vapor phase because its pressure dependence is reasonable. This group, however, has not been included in the fit.

I.2. Effect of Pressure Upon Gas Solubility

In general, there are only two types of experimental studies of gas solubilities: those in which the concentration has been measured isothermally at different pressures and those in which only a few points are measured at the same temperature, usually at almost the same pressure. For those in the first group, the variation of the solubility with the pressure can be an artifact. Hence, in order to obtain k^0 from the first group a direct extrapolation of the data to the vapor pressure of water at the temperature of the experiment is graphically performed.

In the cases where one or only a few points are available at one temperature, the partial molar volume of the solute and its T and P dependence has to be known in order to calculate k^0 from Eq. (1).

It has been shown by Fernández Prini and Japas,¹⁵ that by using a perturbation method, the hard-sphere equivalent diameter of the solute and its temperature dependence and the properties of the pure solvent, V_2^0 can be calculated as a function of T and P.

No reliable hard-sphere equivalent diameters and their corresponding temperature dependence are available for the system CO_2 -H₂O. Thus, the experimentally available data for V_2 in this system obtained by Malinin⁴⁵ and by Crovetto and Wood⁴⁶ are considered. We used them to calculate the needed V_2 in Eq. (1).

Appendix II. Fitting Procedure Employed to Calculate the Temperature Dependence of Henry's Constant

Group A, low temperature, low pressure, was fitted to equation P3. Group C, high temperature, any pressure, was fitted to equations P3 + b, KD, DEN*2, and T*(1/3). The parameter adjustment was done by a least squares procedure that minimizes least squares differences in $\ln k^0$.

For the polynomials in the inverse of the temperature, P3, P3 + b, and T*(1/3), it was tested that further increase in the number of parameters used was not statistically significant. Points with residuals bigger than 2 standard deviations, σ , were rejected. The rejection procedure was stopped when no significant improvement of the σ of the fit was attained by further point rejection. This was achieved in the fourth iteration for group A and in the third iteration for group C.

In the low temperature fit, after the fourth iteration, the deviation plot was analyzed and sources that agreed with the rest of the measurements but did only contribute with a larger scatter, were rejected. [Novak *et al.*, NOV(61), and Verdet *et al.*, VE(855)].

No weighting was attempted.