

# The Solubility of Carbon Dioxide in Water at Low Pressure

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The system carbon dioxide-water is of great scientific and technological importance. Thus, it has been studied often. The literature for the solubility of carbon dioxide in water is vast and interdisciplinary. An exhaustive survey was conducted and approximately 100 experimental investigations were found that reported equilibrium data at pressures below 1 MPa.

A model based on Henry's law was used to correlate the low pressure data (those up to 1 MPa). The following correlation of the Henry's constants (expressed on a mole fraction basis) was developed

$$\ln(H_{21}/\text{MPa}) = -6.8346 + 1.2817 \times 10^4/T - 3.7668 \times 10^6/T^2 + 2.997 \times 10^8/T^3$$

The correlation is valid for  $273 < T < 433$  K ( $0 < t < 160$  °C) where  $T$  is in K. Any experimental data that deviated significantly from this model were duly noted.

Key words: carbon dioxide; CO<sub>2</sub>; Henry's Law; H<sub>2</sub>O; solubility; water.

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## Nomenclature

List of Tables		Nomenclature	
1. Experimental investigations of the solubility of carbon dioxide in water .....	1203	$A_i$	coefficients in Henry's constant correlation
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3. Calculated solubilities of carbon dioxide in water at various total pressures .....	1208	$\hat{f}$	fugacity of a component in a mixture
4. Calculated solubilities of carbon dioxide in water at various carbon dioxide partial pressures .....	1208	$H_{21}$	Henry's constant for solute 2 in solvent 1
		NP	number of points
		$P$	total pressure
		$P^\circ$	vapor pressure
		$Q$	quality
		$R$	gas constant
		$T$	absolute temperature
		$t$	Celsius temperature
		$x$	mole fraction in liquid
		$y$	mole fraction in vapor
		$\Delta C_p$	change in heat capacity
		$\Delta_{\text{soln}}H$	enthalpy of solution
		$\phi$	fugacity coefficient for component in mixture

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## Subscripts

1	component 1, solvent, water
2	component 2, solute, carbon dioxide

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## 1. Introduction

The system carbon dioxide-water is important to virtually all branches of science, both physical and biological. As such, the solubility of carbon dioxide in water is one of the most often studied phenomena in all of physical chemistry. A cursory review of the list of references reflects this wide interest in the solubility of CO<sub>2</sub> in water. Papers listed are from journals that deal with pure chemistry, geochemistry, chemical engineering, physics and many branches of biological sciences.

Initially, it was the purpose of this investigation to assemble all the experimental solubility data for this system. An exhaustive literature search was undertaken to find all the experimental investigations of carbon dioxide-water. This proved to be a very large task indeed and the problem of reducing these data to a digestible form was formidable. Also, there remains some disagreement between the data for this system at high pressure [for example see Tödheide and Franck (1963) and Takenouchi and Kennedy (1964)]. For these reasons, it was decided to limit this investigation to the low pressure region (pressures less than 1 MPa). Even with this limitation, over eighty papers reporting experimental data were compiled. This set of data was reduced to Henry's constants, which were then compared and correlated. A recommended equation for Henry's constant as a function of temperature was obtained.

## 2. Literature Review

Solubility measurements for carbon dioxide in water date back at least as far as the work of Henry (1803) in which he postulated his now-famous law of solubility. However, the first accurate solubility data begin to appear about half way through the nineteenth century with the pioneering work of Bunsen (1855a,b,c). This review begins with his work and ends at about 1990.

Table 1 lists chronologically the investigations examined in this study. Included in this table are the pressure and temperature ranges for each study. Because of the model used to correlate the solubility, pressures were limited to 1 MPa. Many studies listed extend to more severe conditions than those given; only the region of interest to this study is listed. Also listed in Table 1 are the number of experimental points for each study (NP) and a grade assigned to that work (Q). The grade will be discussed in more detail in a subsequent section. It is sufficient at this point to note that a grade of 1 is superior and a grade of 5 is poor.

In many cases there was great difficulty determining whether the data were reported at a given total pressure or CO<sub>2</sub> partial pressure. *If it could not be determined which pressure was used, then it was assumed that it was the total pressure.* The significance of the difference between total and partial pressure will be discussed in more detail later in the paper.

In the past, it was common to take several measurements at near atmospheric pressure and then correct

them to 1 atm by assuming the strict Henry's law applied (that is, it was assumed that the solubility was directly proportional to the partial pressure of the gas). Other studies involved many measurements, but only the average value was reported. No works were rejected for these reasons. The age of the data was not a factor in determining its quality either. Also, there are about as many different methods for measuring the solubility as there are investigations. The technique employed was not a factor in considering the quality of the data. This is not to imply that all methods are equal, just that it was not factored into our grading system.

In compiling the literature review, the review papers of Markham and Kobe (1941a), Battino and Clever (1966) and Wilhelm *et al.* (1977) and the compilations of Linke (1958), Stephen and Stephen (1963) and Staples *et al.* (1986) were very useful. However, this survey is more complete than those mentioned.

There is also a vast literature of experimental studies at higher temperature and higher pressure. One reason why this study was restricted to pressures less than 1 MPa was because this was believed to be a significant portion of the rather large database.

## 3. The Solubility Model

Recently Carroll and Mather (1989) employed a simple extension of Henry's law to model accurately the solubility of hydrogen sulfide in water. Since the solubility of carbon dioxide in water is about the same magnitude as that of hydrogen sulfide, this model will be employed here as well. The model begins with the equality of fugacities and involves a few simplifying assumptions. It is assumed (1) that the activity coefficients for both the solvent and the solute are unity and (2) the Poynting correction is negligible. The solvent is modeled as

$$x_1 P_1^s = y_1 \hat{\phi}_1 P \quad (1)$$

and the solute

$$x_2 H_{21} = y_2 \hat{\phi}_2 P \quad (2)$$

where  $x_i$  is the mole fraction of component  $i$  in the liquid,  $y_i$  is the mole fraction of component  $i$  in the vapor,  $P_1^s$  is the vapor pressure of the pure solvent,  $H_{21}$  is the Henry's constant,  $\hat{\phi}_i$  is the fugacity coefficient for component  $i$  where component 1 is water and 2 is carbon dioxide and  $P$  is the total pressure. The product  $y_2 P$  is the partial pressure of CO<sub>2</sub>, which will be used in the discussion that follows.

The total pressure is limited to about 1 MPa because this model neglects liquid phase non-idealities, which at pressures greater than 1 MPa begin to become important. At higher pressures, the solubility of carbon dioxide increases to the point where the activity coefficients can no longer be neglected. Also, above 1 MPa, the Poynting correction (the effect of pressure on the reference fugacity) becomes important. The error arising from neglecting

TABLE 1. Experimental investigations of the solubility of carbon dioxide in water

Source	Temp (°C)	Press (kPa)	NP	Q	Source	Temp (°C)	Press (kPa)	NP	Q
Bunsen (1855a,b,c)	0-20	101	6	2	Enders <i>et al.</i> (1956a,b)	15-20	101	2	2
Khanikof and Louguinine (1867)	15	93-414	10	4	Loprest (1957)	20-60	101	?	G
Buchanan (1874)	10-13	55-105	15	1	Shchennikova <i>et al.</i> (1957)	20-75	103-140	5	1,5
Wroblewski (1882,1883)	0-12	101-1013	6	3	Ellis (1959)	114-163	500-800	4	5
Müller (1889)	19	104	4	2	Bartels and Wrbitzky (1960)	15-38	101	6	1
Bohr and Bock (1891)	37-100	100-187	2	5,5	Novák <i>et al.</i> (1961)	11-40	13-97	54	2,3
Setchenow (1892)	15	101	1	1	Cox and Head (1962)	20-30	103-108	6	2
Prytz and Holst (1895)	0	101	1	2	Siejsö (1962)	38	101	1	4
Bohr (1899)	0-61	101-122	15	1,2	Austin <i>et al.</i> (1963)	20-38	101	5	1
Hantzsch and Vagt (1901)	0-90	10-78	8	5,5	Yeh and Peterson (1964)	25-45	101	4	2
Just (1901)	25	101	1	1	Davies <i>et al.</i> (1967)	20-25	101	2	1
Geffken (1904)	15-25	101	2	1	Robb and Zimmer (1968)	20-27	101	2	4
Christoff (1905)	15.5	96	1	1	Böxkes and Emig (1969)	25	101	?	G
Findlay and Creighton (1910)	25	99-180	12	1	Matous <i>et al.</i> (1969)	30-80	930-1005	3	1,1
Usher (1910)	20	101	1	2	Salomaa <i>et al.</i> (1969)	25	101	1	1
Findlay and Shen (1911)	25	101	1	1	Tokunaga <i>et al.</i> (1969)	10-40	101	4	2
Findlay and Shen (1912)	25	100-180	12	1	Onda <i>et al.</i> (1970)	25	104	1	1
Findlay and Williams (1913)	25	36-102	10	2	Stewart and Munjal (1970)	0-10	1013	3	3
Findlay and Howell (1915)	25	36-132	18	2	Barton and Hsu (1971)	0-40	101-109	3	2
Hammel (1915)	15	103	5	2	Gerecke and Biturich (1971)	25	101	1	1
Piazza (1918)	50	108	1	5	Hayduk and Malik (1971)	25	104	1	1
Hähnel (1920)	0-15	101-1013	5	4	Li and Tsui (1971)	0-30	101	5	2
Kunerth (1922)	18-36	101	8	1	Murray and Riley (1971)	1-35	101-107	8	2
Metschl (1924)	25	101	1	5	Perez and Sandall (1974)	24-35	104-107	3	1
Buch (1925)	18	2	10	5	Sada <i>et al.</i> (1974)	25	101	1	2
Gatterer (1926)	5-25	101	5	1	Weiss (1974)	21	101	1	1
Wolf and Krause (1927)	20	101	1	5	Tokunaga (1975)	0-40	101	4	2
Van Slyke <i>et al.</i> (1928)	38	101	1	3	Truchot (1976)	15	101	1	1
Morgan and Pyne (1930)	25	101	1	1	Yasunishi and Yoshida (1979)	15-35	101	3	2
Morgan and Maass (1931)	0-25	8-113	19	3	Wasmund and Bultmann (1980a,b)	0-60	100-900	65	4,3
Kobe and Williams (1935)	25	101	1	1	Cargill and Macphee (1981a,b)	4-63	101	16	3,5
Showalter and Ferguson (1936)	15	101	1	2	Won <i>et al.</i> (1981)	25	104	1	1
Kiss <i>et al.</i> (1937)	0-25	101-104	3	2	Zawisza (1981) and Zawisza and Malesinska (1981)	50-150	150-890	8	1
Orcutt and SeEVERS (1937)	25	101	1	1	Gillespie and Wilson (1982)	31-121	689	5	4,5
Zel'vinskii (1937)	0	105-1013	3	3	Takahashi <i>et al.</i> (1982)	25	101	1	2
Curry and Hazelton (1938)	22	100	1	4	Hikita <i>et al.</i> (1985)	25	104	1	1
Van Slyke (1939)	23-26	101	6	1	Kruus and Hayes (1985)	25	101-104	3	1
Markham and Kobe (1941b)	0-40	101	4	2	Postigo and Katz (1987)	15-35	101	5	2
Harned and Davis (1943)	0-50	101	17	1	Müller <i>et al.</i> (1988)	100-160	325-940	8	1
Kobe and Mason (1946)	25	104	1	2	Versteeg and Van Swaaij (1988)	18-87	103-164	18	2,1
Essery and Gane (1952)	0	101	1	2					
Morrison and Billett (1952)	13-75	102-140	19	2,2					
Gjaldbæk (1953)	25	101	1	1					
Bartholomé and Friz (1956)	10-30	103-106	3	1					

NP - Number of data points.

Q - Grade assigned to data, see Table 2 and text.

the Poynting term at 1 MPa is estimated to be about 1%. This error continues to increase with increasing pressure. Thus at pressures greater than 1 MPa, neglecting the liquid phase non-idealities results in a significant error.

To implement the model, the vapor pressure of water is taken from Haar *et al.* (1984). The fugacity coefficients for a component in a gaseous mixture are calculated using the Redlich-Kwong (1949) equation of state. Thus for an experimental point consisting of the pressure, temperature and solubility, an iterative procedure is used to calculate the Henry's constant and the vapor composition. There are almost as many solubility units as there are investigators. Thus, all solubility data were converted to mole fraction in order to use Eqs. (1) and (2).

Henry's constants calculated from the experimental data were correlated using a polynomial in reciprocal temperature.

$$\ln H_{21} = \sum_{i=0}^N A_i (1000/T)^i \quad (3)$$

Initially a least squares regression was applied to all the calculated Henry's constants. Four terms ( $N = 3$ ) were sufficient to fit accurately the Henry's constants. Any values that deviated significantly from the regression were rejected and another regression was performed. Typically all the values from a given author were rejected if the average error was greater than 5%. An exception to this was the data of Novák *et al.* (1961). In general, their values are in good agreement with the exception of four points (usually the lowest solubility for a given temperature),

which were in serious error and thus rejected. After the second regression, Eq. (3) becomes

$$\ln(H_{21}/\text{MPa}) = -6.8346 + 1.2817 \times 10^4/T - 3.7668 \times 10^6/T^2 + 2.997 \times 10^8/T^3 \quad (4)$$

where  $T$  is in K. Henry's constants are plotted in Fig. 1. On this figure a distinction is made between those values deemed to be acceptable and those that are not. Since there are so many points no attempt was made to indicate the source of all of the data. However, a few of the poorest data have been identified. Typical of the solubility of a gas in water, the Henry's constant goes through a maximum. From Eq. (4) the maximum is at 148 °C.

Some data points on Fig. 1 have been denoted as "rejected data" in spite of appearing to be in relatively good agreement with the majority of the data. This was done because they belong to a set of data that were deemed to be inferior on the whole.

When carbon dioxide dissolves in water it forms a weak acid. The ionization is quite small and has been neglected in this study.

### 3.1. Grading the Data

By comparing the calculated Henry's constant with those from the correlation, the experimental data were assigned a grade. Table 2 summarizes the grading system. The system was somewhat arbitrarily separated into a low temperature ( $t < 50$  °C) region and a high temperature ( $t > 50$  °C) region. This division was made partially in recognition of the fact that solubility measurements are more difficult to make at higher temperatures. Most of the data are at temperatures less than 50 °C. Works that span both regions were assigned two grades, the first for the low temperature region and the second for the high. Loprest (1957) and Bökkes and Emig (1969) report only graphical results for their solubility measurements and thus were given a grade of G. In the low temperature region ( $t < 50$  °C) most of the works received a grade of 1 or 2 and therefore are of high quality. It is somewhat surprising that some of the older data received good grades. The data of Bunsen (1855a,b,c), often stated to be of historic value only, are in good agreement with the model and hence with the more modern data receiving a grade

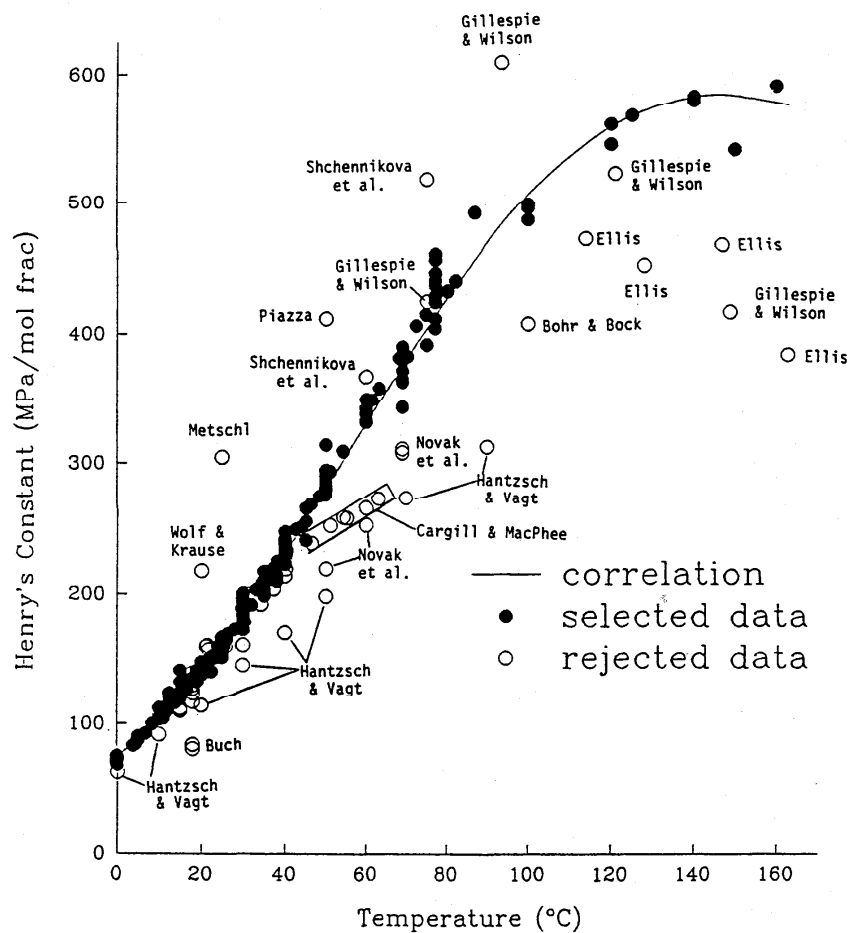


FIG. 1. Henry's Constant for carbon dioxide in water.

TABLE 2. The grading system

Grade	0 < t < 50 °C	50 < t < 163 °C
1	e < 1.5	e < 2.5
2	1.5 < e < 3.0	2.5 < e < 6.0
3	3.0 < e < 5.0	6.0 < e < 10.0
4	5.0 < e < 10.0	10.0 < e < 15.0
5	e > 10.0	e > 15.0
G	Only graphical data given	

$$e = \frac{\sum_{i=1}^{NP} \text{abs}(\text{calc} - \text{exp})/\text{calc} \times 100\%}{NP}$$

where  $e$  is the average absolute percentage error in the Henry's constant.

of 2. Also, the data of Bohr (1899) agree very well with both the model and modern data. His data received a grade of 1 in the low temperature region. The values in Lange's Handbook (Dean, 1985), an often quoted source for chemical data, are from Bohr (1899) although they are not referenced as such. The table of smoothed values from Bohr (1899) is reproduced in Lange's Handbook. These values also appear in older editions of the CRC Handbook (Hodgman, 1960), another important source of chemical data; but they have been deleted from more recent editions (Weast, 1983). The source of the few values that appear in the later editions of the CRC Handbook is unclear. However, if the total pressure for these data is 101.325 kPa, then they are in good agreement with this model.

On the other hand, the data of Bohr and Bock (1891), Hantzsch and Vagt (1901), Piazza (1918), Metschl (1924), Buch (1925) and Wolf and Krause (1927) received a grade of 5 and are judged to be in error by a significant amount. The data of Khanikof and Louguinine (1867), Hähnel (1920), Curry and Hazelton (1938), Siejsö (1962), Robb and Zimmer (1968), Wasmund and Bultmann (1980a,b) and Wilson and Gillespie (1982) received a grade of 4 and thus are of low quality.

Of the data in the range of temperature  $50 < t < 100$  °C, Hantzsch and Vagt (1901), Shchennikova *et al.* (1957) and Cargill and MacPhee (1981a,b) received grades of 5. The error in these data is clearly shown on Fig. 1. However, the low temperature data of Shchennikova *et al.* (1957) were in good agreement with the model receiving a grade of 1. The majority of the other data in this range receive grades of 1 or 2. Most of these data are at temperatures below 80 °C; very few low pressure data exist between 80 and 100 °C.

At 100 °C and above the data of Müller *et al.* (1988), Zawisza (1981) and Zawisza and Malesinska (1981) were concluded to be the most reliable. [Note the data of Zawisza (1981) are repeated in Zawisza and Malesinska (1981).] The only other data in this region are those of Bohr and Bock (1891), Ellis (1959) and Gillespie and Wilson (1982). A single point from Bohr and Bock (1891) is at 100 °C. The Henry's constant calculated from this point is in poor agreement with the more reliable data. The data of Ellis (1959) are, by his own admission, "not of high precision". Since the data of Gillespie and Wilson

(1982) show significant deviations at low temperature, it is a good probability that their high temperature data are equally poor. As a result, when the data of Bohr and Bock (1891), Ellis (1959) and Gillespie and Wilson (1982) are compared with those of Müller *et al.* (1988), Zawisza (1981) and Zawisza and Malesinska (1981) the former must be given grades of 5.

### 3.2. Enthalpy of Solution

The enthalpy of solution can be estimated from the Henry's constants via the following approximate relation (Sherwood and Prausnitz, 1962)

$$[\partial \ln H_{21}/\partial(1/T)] = \Delta_{\text{soln}}H/R \quad (5)$$

where  $\Delta_{\text{soln}}H$  is the enthalpy of solution and  $R$  is the gas constant (8.314 J/mol K). Differentiating Eq. (4) yields

$$\Delta_{\text{soln}}H = 106.56 - 6.2634 \times 10^4/T + 7.475 \times 10^6/T^2 \quad (6)$$

where  $\Delta_{\text{soln}}H$  is in kJ/mol. Berg and Vanderzee (1978) measured the enthalpy of solution of CO<sub>2</sub> in water to be  $-19.57 \pm 0.17$  kJ/mol at 25 °C. Gill and Wadsö (1982) also measured the enthalpy of solution at 25 °C; they obtained a value of  $-19.67 \pm 0.10$  kJ/mol. These values were obtained calorimetrically and not from solubility data (as many of the enthalpies of solution found in the literature are). The value calculated from Eq. (6) is  $-19.43$  kJ/mol, which is very good agreement. This is a test of the consistency of the correlation of the Henry's constants. Significant difference between the measured and estimated enthalpy of solution would raise some doubt about the validity of the correlation used for the temperature dependence of Henry's constant.

It is interesting to note that at about 148 °C Eq. (6) predicts that the enthalpy of solution is zero. This is the point where the Henry's constant is a maximum. At higher temperatures, the enthalpy of solution is a positive quantity.

The heat capacity of the CO<sub>2</sub> (aq) species can then be estimated by taking the temperature derivative of the enthalpy of solution

$$(\partial \Delta_{\text{soln}}H/\partial T) = \Delta C_p \quad (7)$$

where

$$\Delta C_p = C_p [\text{CO}_2 (\text{aq})] - C_p [\text{CO}_2 (\text{g})] \quad (8)$$

Thus

$$\Delta C_p = 6.2634 \times 10^7/T^2 - 1.4950 \times 10^{10}/T^3 \quad (9)$$

where  $\Delta C_p$  is in J/mol K. Barbero *et al.* (1983) measured  $C_p [\text{CO}_2 (\text{aq})]$  using a flow microcalorimeter and obtained a value of  $243 \pm 7$  J/mol K at 25 °C. From Eqs. (8) and (9) and using  $C_p [\text{CO}_2 (\text{g})] = 37.12$  J/mol K (McBride and Gordon, 1961) one obtains  $C_p [\text{CO}_2 (\text{aq})] = 178$  J/mol K.

There is no reason to doubt the accuracy of the experimental result. However, rather than indicating a major problem with the correlation of the Henry's constant, the best explanation for this fairly poor agreement is that differentiating the Henry's constant twice is a poor method for estimating heat capacities.

#### 4. Calculated Solubilities

The model was then used to calculate the solubility of carbon dioxide in water. In this case, given the temperature and pressure, the Henry's constant is calculated using Eq. (4), the vapor pressure of water is obtained from Haar *et al.* (1984) and the fugacity coefficients are calculated using the Redlich-Kwong (1949) equation. Using an iterative procedure, Eqs. (1) and (2) are solved for the liquid and vapor compositions ( $x_1$ ,  $x_2$ ,  $y_1$  and  $y_2$ ).

Figure 2 shows the solubility at a total pressure of 101.325 kPa. This figure is split into two parts. Experimental data from ten sources thus can clearly be compared with the model. Most of the data shown on Fig. 2 received a grade of 1 or 2. The exception is the data of Cargill and MacPhee (1981a,b), which show significant deviation from the model. Although their data appear to be at a CO<sub>2</sub> partial pressure of 101.325 kPa, their paper clearly states that they are at a total pressure of 101.325 kPa. As noted earlier, their high temperature data received a grade of 5. The reason is clear from this graph.

Figure 3 shows the solubility at a CO<sub>2</sub> partial pressure of 101.325 kPa. Also shown on this plot are experimental data from four sources. Calculation of the solubility at a CO<sub>2</sub>-partial pressure of 101.325 kPa requires a second iterative loop. Basically, the solubility is calculated as before, except now the pressure is adjusted until  $y_2P$  equals 101.325 kPa. Except for the high temperature values from Shchennikova *et al.* (1957), the agreement between the model and the experimental values is good. It is clear why the high temperature data of Shchennikova *et al.* (1957) received a grade of 5. Also, there is some confusion as to whether the data of Morrison and Billett (1952) are at 101.325 kPa total pressure or partial. From Fig. 3 and our interpretation of their paper, the data of Morrison and Billett (1952) are at 101.325 kPa CO<sub>2</sub> partial pressure.

From Figs. 2 and 3, clearly there is some difference between the solubility at a total pressure of 101.325 kPa and a CO<sub>2</sub>-partial pressure of 101.325 kPa. At low temperature this difference is small because the vapor pressure of water is very small at these temperatures. However, the difference in the solubilities increases with increasing temperature. At 25 °C the difference is 3.2%, at 50 °C it is 13.8% and at 75 °C it is 61.2%. At 100 °C and a total pressure of 101.325 kPa the solubility is, by definition, zero. Above 100 °C and a total pressure of 101.325 kPa only vapor exists. However, at partial pressures of 101.325 kPa the solubility tends to level off (about 0.02 mol%) at temperatures above 100 °C. As noted earlier, the Henry's constant correlation shows a maximum at 148 °C whereas the solubility curve has a very shallow minimum at 149 °C.

Over the range of temperature 130 to 160 °C the calculated solubility changes by less than 2%. The reason why the minimum solubility and maximum Henry's constant do not exactly correspond is a result of the effect of fugacity. The fugacity of the CO<sub>2</sub> in the gas is different when the partial pressure is 101.325 kPa than it is at infinite dilution.

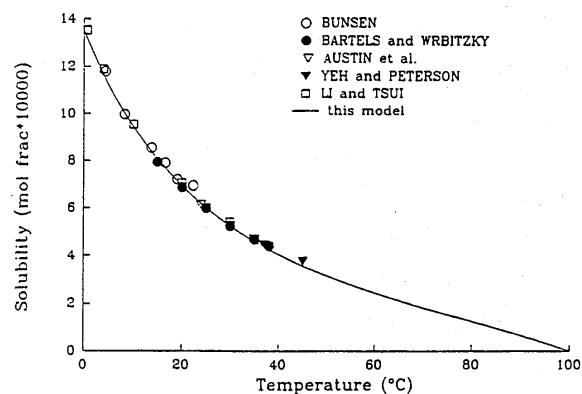
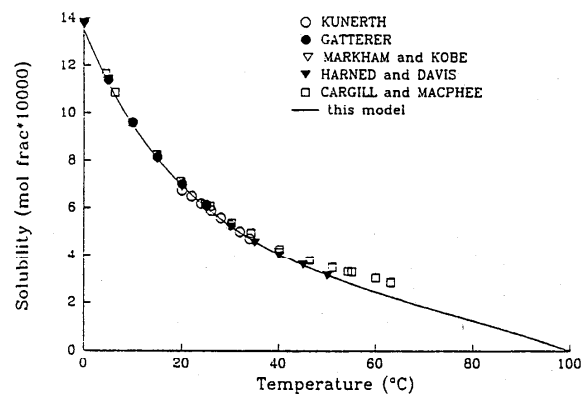


FIG. 2. The solubility of carbon dioxide in water at a total pressure of 101.325 kPa.

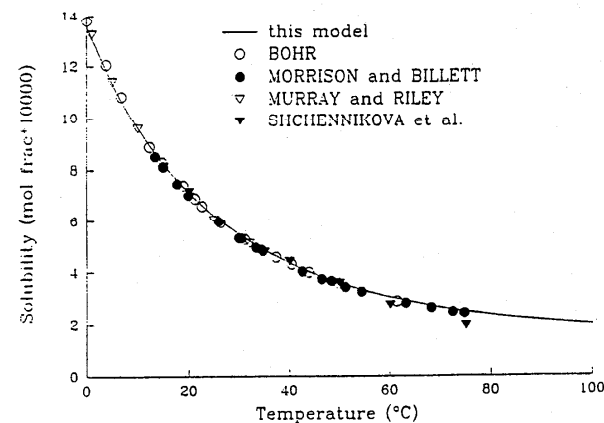


FIG. 3. The solubility of carbon dioxide in water at a carbon dioxide partial pressure of 101.325 kPa.

Figure 4 shows the effect of pressure as well as temperature on the solubility. Eight isotherms from 0 to 80 °C are shown on this plot with experimental data from five sources. Higher temperatures will be given later. For clarity this plot is presented using log-log axes. Although there is some scatter, the model is a good fit of the experimental data.

Figure 5 shows the solubility for five isotherms from 100 to 160 °C and experimental data from three sources. As noted earlier, the data of Zawisza and Malesinska (1981) and Müller *et al.* (1988) are considered to be the most reliable in this range of temperature. The point from Bohr and Bock (1891) is also shown on Fig. 5. Although it appears to be in good agreement with the model, it is significantly different. Note that although the Henry's constant at 160 °C is less than at 150 °C, the solubility at 160 °C is less than at 150 °C for a given total pressure.

The solubility of carbon dioxide in water for various total pressure and CO<sub>2</sub> partial pressure have been tabulated in Tables 3 and 4. These values were obtained using the model outlined above and are provided for quick reference. They should not be considered as a substitute for experimental data.

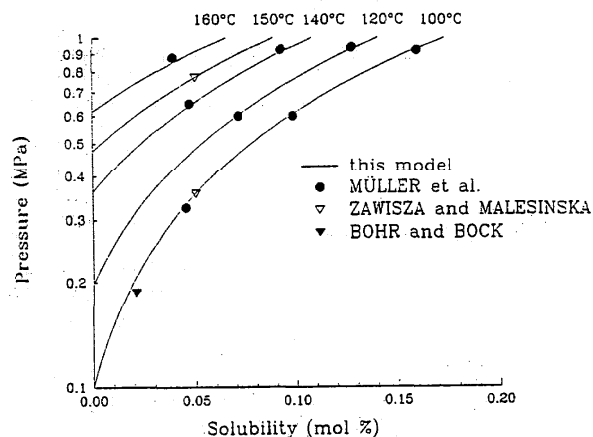


FIG. 5. The solubility of carbon dioxide in water from 100 to 160 °C.

#### 4.1. Vapor Phase Compositions

Few measurements of the vapor phase compositions exist at low pressure. There are a few points from Wiebe and Gaddy (1941), Zawisza and Malesinska (1981) and

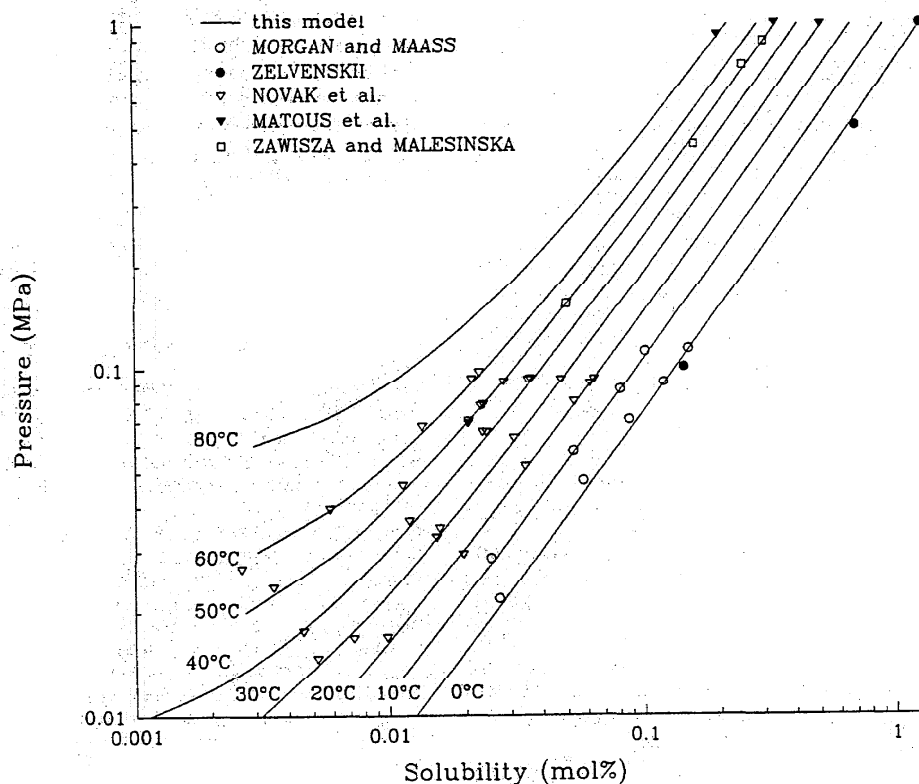


FIG. 4. The solubility of carbon dioxide in water from 0 to 80 °C.

TABLE 3. Calculated solubilities for carbon dioxide in water at various total pressures

Temperature (°C)	Solubility of CO in water at various total pressures (Solubility in mole fraction $\times$ 1000, pressure in kPa)					
	50	101.325	200	500	750	1000
0	0.670	1.362	2.68	6.58	9.72	12.75
10	0.479	0.962	1.90	4.68	6.93	9.11
20	0.340	0.704	1.398	3.47	5.14	6.77
25	0.291	0.609	1.216	3.02	4.49	5.92
30	0.251	0.531	1.065	2.66	3.95	5.22
40	0.186	0.409	0.835	2.11	3.14	4.16
50	0.135	0.319	0.669	1.72	2.57	3.41
60	0.091	0.247	0.544	1.435	2.16	2.88
70	0.047	0.185	0.444	1.220	1.86	2.48
80	0.006	0.127	0.357	1.050	1.62	2.18
90	...	0.067	0.277	0.908	1.426	1.94
100	...	...	0.195	0.782	1.265	1.74
110	...	...	0.106	0.662	1.119	1.57
120	...	...	0.003	0.537	0.977	1.412
130	...	...	...	0.400	0.828	1.253
140	...	...	...	0.238	0.662	1.083
150	...	...	...	0.042	0.466	0.887
160	...	...	...	...	0.277	0.653

TABLE 4. Calculated solubilities for carbon dioxide in water at various CO<sub>2</sub> partial pressures

Temperature (°C)	Solubility of CO in water at various partial pressures (Solubility in mole fraction $\times$ 1000, pressure in kPa)			
	50	101.325	200	500
0	0.671	1.355	2.66	6.52
10	0.477	0.963	1.89	4.65
20	0.353	0.713	1.400	3.45
25	0.308	0.622	1.223	3.01
30	0.271	0.548	1.077	2.66
40	0.216	0.437	0.858	2.12
50	0.178	0.359	0.706	1.75
60	0.150	0.304	0.598	1.480
70	0.131	0.264	0.520	1.288
80	0.116	0.236	0.463	1.148
90	0.106	0.214	0.422	1.046
100	0.098	0.199	0.391	0.971
110	0.093	0.188	0.370	0.917
120	0.089	0.180	0.354	0.880
130	0.086	0.175	0.345	0.856
140	0.085	0.172	0.339	0.844
150	0.085	0.172	0.338	0.841
160	0.085	0.173	0.340	0.846

Müller *et al.* (1988). The Wiebe and Gaddy (1941) vapor compositions are only at 101.325 kPa, although they have other data outside the range of this investigation. The values of Zawisza and Malesinska (1981) and Müller *et al.* (1988) with the prediction from this model are shown on Fig. 6. This represents a "true" prediction since the experimental vapor compositions were not used in the development of the model. The agreement between the model and the experimental data is good and hence, in some small measure, verifies the applicability of the model. Note, the curves intersect the  $x_1 = 1$  axis at the vapor pressure of water.

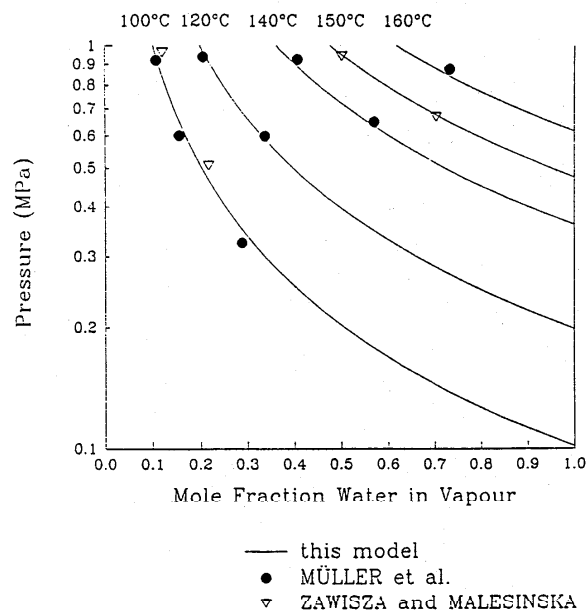


FIG. 6. Water content of the vapor in equilibrium with carbon dioxide solutions.

## 5. Conclusions

A large data base consisting of all the low pressure ( $P < 1$  MPa) solubility data for carbon dioxide in water was assembled. Using a model based on Henry's law the data were compared and graded. Several studies were shown to be of poor quality. As a result of this investigation a new correlation of the low pressure solubility was developed.

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