Carbon dioxide in water equilibrium

1. Introduction

Carbon dioxide does dissolve in water, however the system is somewhat complex[1].

First the CO_2 dissolves according to:

(1) $CO_2\ (g) \Leftrightarrow CO_2\ (l)$

At room temperature, the solubility of carbon dioxide is about 90 cm^3 of CO_2 per 100 ml water ($c_l/c_g = 0.8$).

Any water-soluble gas becomes more soluble as the temperature decreases, due to the thermodynamics of the reaction: GAS (l) ⇔ GAS (g). The entropy change, ΔS, of this reaction is positive because the gas molecules are less constrained than the gas molecules in solution. The change in Free energy of reaction with an increase in temperature is $-\Delta S$. This effect is particularly large for gases like CO_2 that undergo specific reactions with water.

Equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid.

(2) $CO_2\ (l) + H_2O\ (l) \Leftrightarrow H_2CO_3\ (l)$

This reaction is kinetically slow. At equilibrium, only a small fraction (ca. 0.2 - 1%) of the dissolved CO_2 is actually converted to H_2CO_3. Most of the CO_2 remains as solvated molecular CO_2. As equation:

$$K_r = \frac{[H_2CO_3]}{[CO_2]_l} \approx 1.7.10^{-3}$$

In fact, the pK_a most reported for carbonic acid ($pK_{a1} = 6.37$) is not really the true pK_a of carbonic acid. Rather, it is the pK_a of the equilibrium mixture of CO_2 (l) and carbonic acid. Carbonic acid is actually a much stronger acid than this, with a true pK_{a1} value of 3.58. However these values are also temperature dependent.

Carbonic acid is a weak acid that dissociates in two steps[2].

(3) $H_2CO_3 + H_2O \Leftrightarrow H_3O^+ + HCO_3^-$ pK_{a1} (25 °C) = 6.37

(4) $HCO_3^- + H_2O \Leftrightarrow H_3O^+ + CO_3^{2-}$ pK_{a2} (25 °C) = 10.25

Note that these carbonate anions can interact with the cations present in the water to form insoluble carbonates. For instance, if Ca^{2+} is present limestone, $CaCO_3$ is formed and if Mg^{2+} is present $MgCO_3$ is formed. The formation of these deposits is an additional driving force that can pull the equilibrium more to the right resulting in acidification of the water[2].

(5) $Ca^{2+} + CO_3^{2-} \Leftrightarrow CaCO_3\downarrow$ $S = 4.96 \times 10^{-9}$ (S = solubility constant)

(6) $Mg^{2+} + CO_3^{2-} \Leftrightarrow MgCO_3\downarrow$ $S = 6.82 \times 10^{-6}$

The above presented more schematically:

$$CO_2(g) \Leftrightarrow CO_2\ (l) \overset{+ H_2O}{\Leftrightarrow} H_2CO_3 \overset{+ H_2O}{\Leftrightarrow} \underset{+ H_3O^+}{HCO_3^-} \overset{+ H_2O}{\Leftrightarrow} \underset{+ H_3O^+}{CO_3^{2-}} \overset{+ Ca^{2+}}{\Leftrightarrow} CaCO_3\downarrow$$

Note that the reverse is also true and that the scheme represents the solubility of $CaCO_3$ in an acidic solution resulting in the liberation of CO_2 in the atmosphere.

2. Deriving [H_2CO_3]

If we assume CO_2 is a simple gas we can apply Henry's law that describes the equilibrium between vapor and liquid. Thus:

$p_{CO2} = K \,.\, x_{CO2}$

where p_{CO2} is the partial pressure of the gas in the bulk atmosphere (Pa), K is a constant (Pa) and x_{CO2} is the equilibrium mole fraction of solute in liquid phase.

The solubility of CO_2 is temperature dependent, as shown in Table 1: Solubility of CO2 at a partial pressure for CO2 of 1 bar abs[3].

Table 1: Solubility of CO_2 at a partial pressure for CO_2 of 1 bar abs[3].

Temperature (oC)	0	10	20	30	40	50	80	100
Solubility (cm^3 CO_2/g water)	1.8	1.3	0.88	0.65	0.52	0.43	0.29	0.26

Furthermore, as stated above, CO_2 reacts with the water on dissolution and therefore one would expect that Henry's law has to be modified.

However, according to Carrol and Mather [4] a form of Henry's law can be used for modeling the solubility of carbon dioxide in water for pressures up to about 100 MPa, as can be seen in Figure 1: Henry's Constant for Carbon Dioxide in Water - from Carroll et al. [4].

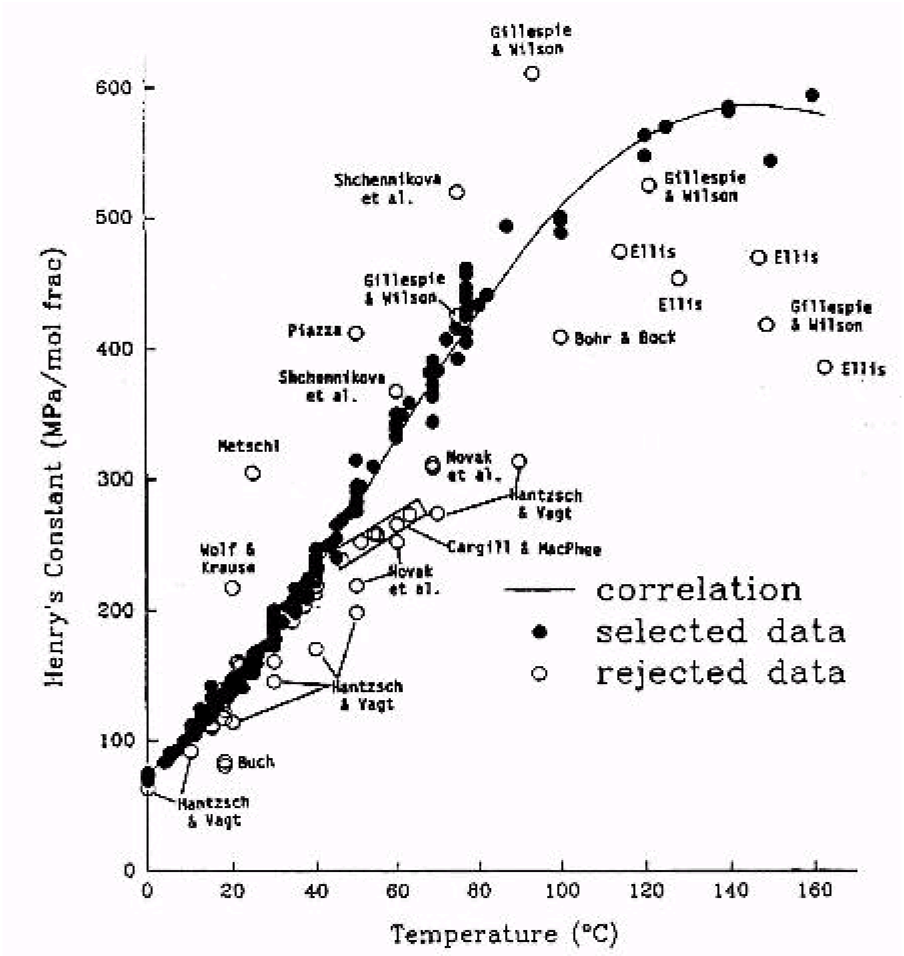

Figure 1: Henry's Constant for Carbon Dioxide in Water - from Carroll et al. [4]

They conclude that the Krichevsky-Kasarnovsky Equation, which can be derived from Henry's Law, can be used to model the system CO_2-H_2O at temperatures below 100 ^oC.

Thus in the range of interest, 20-35 °C, the Henry coefficient for CO_2 in water goes from 150 - 200 MPa/mole fraction

Applying the above to the conditions under investigation:
Temperature range: 20 – 35 °C
Pressure range: 80 – 90 bar
CO_2 concentration in gas phase: 1.3-1.7 mol%

The partial pressure of CO_2 in the gas phase is therefore in the range:
1.3/100 * 80 * 0.1 = 0.104 MPa
1.7/100 * 90 * 0.1 = 0.153 MPa

Applying Henry's Law we calculate a CO_2 mole fraction in water in the range:
x_{low} = 0.104 / 200 = 0.00052
x_{high} = 0.153 / 150 = 0.00102

Converting mole fractions to concentrations:
At 20 °C the molar density of water = 998.21/18.02 = 55.39 mol/l
At 35 °C the molar density of water = 994.37/18.02 = 55.18 mol/l

Thus the CO_2 concentration range in water under these conditions is:
c_{low} = 0.00052 * 55.18 = 0.029 mol/l
c_{high} = 0.00102 * 55.39 = 0.056 mol/l

3. Calculating the pH[5]

The basic equations needed to calculate the pH are derived from equation (3) and (4).

Note: $x = [H_3O^+]$ and $y = [OH^-]$

The protolysis constants:

$$K_{a1} = \frac{x[HCO_3^-]}{[H_2CO_3]} (\approx \frac{x[HCO_3^-]}{[CO_2 + H_2CO_3]} \approx \frac{x[HCO_3^-]}{[CO_2]_l})$$

$$K_{a2} = \frac{x[CO_3^{2-}]}{[HCO_3^-]}$$

Assuming the initial concentration of carbonic acid = c then we derive the steuchiometric relation:

$c = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}]$

The water constant: $x.y = K_w$ and $pK_w = 14$

The electro neutrality equation:
$2[CO_3^{2-}] + [HCO_3^-] + y = x$

We now have 5 equations and 5 unknowns.
From the equilibrium constants we derive

$$[HCO_3^-] = \frac{x[CO_3^{2-}]}{K_{a2}}$$

and

$$[H_2CO_3] = \frac{x^2[CO_3^{\ 2-}]}{K_{a1}K_{a2}}$$

Substituting these into the steuchiometric relation we derive:

$$c = \frac{x^2[CO_3^{\ 2-}]}{K_{a1}K_{a2}} + \frac{x[CO_3^{\ 2-}]}{K_{a2}} + [CO_3^{\ 2-}] = [CO_3^{\ 2-}]\left(1 + \frac{x}{K_{a2}} + \frac{x^2}{K_{a1}K_{a2}}\right) \Rightarrow$$

$$[CO_3^{\ 2-}] = \frac{K_{a1}K_{a2}.c}{x^2 + K_{a1}.x + K_{a1}K_{a2}}$$

$$[HCO_3^{\ -}] = \frac{K_{a1}.x.c}{x^2 + K_{a1}.x + K_{a1}K_{a2}}$$

These equations can be used to calculate in which pH area which CO_2 species dominates as can be seen in Figure 2: pH and CO2 species.

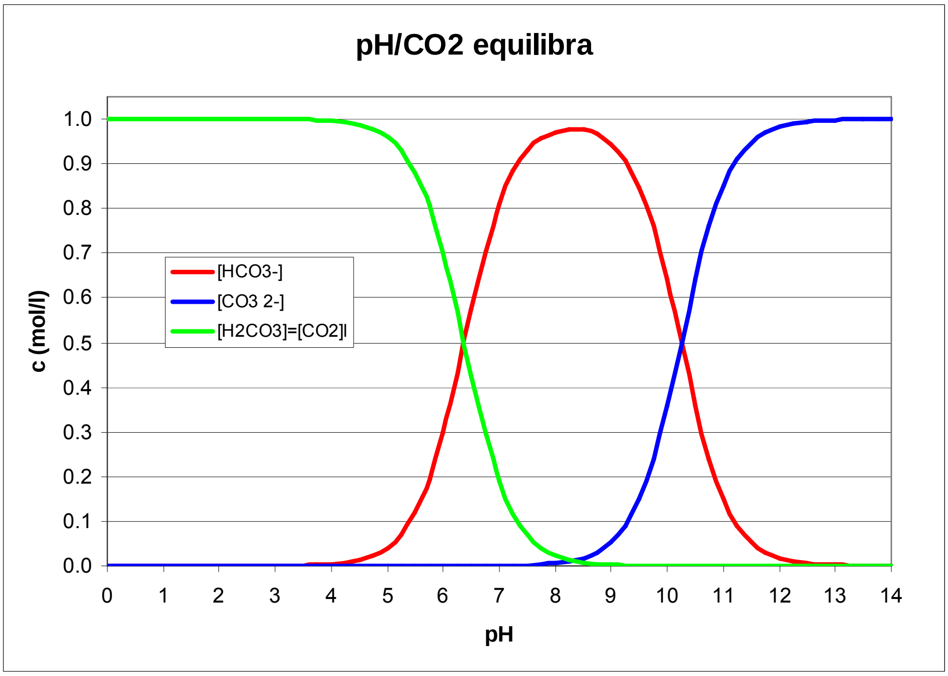

Figure 2: pH and CO_2 species

Substituting these into the electro neutrality equation:

$$2\frac{K_{a1}K_{a2}.c}{x^2 + K_{a1}.x + K_{a1}K_{a2}} + \frac{K_{a1}.x.c}{x^2 + K_{a1}.x + K_{a1}K_{a2}} + y = x \Rightarrow$$

$$c.\frac{2.K_{a1}K_{a2} + K_{a1}.x}{x^2 + K_{a1}.x + K_{a1}K_{a2}} + y = x$$

Combining the above with Kw=x.y we derive a 4th degree equation in x:

$$c.\frac{2.K_{a1}K_{a2} + K_{a1}.x}{x^2 + K_{a1}.x + K_{a1}K_{a2}} + \frac{K_w}{x} = x$$

Compare:

$$\frac{2.K_{a1}K_{a2}+K_{a1}.x}{x^2+K_{a1}.x+K_{a1}K_{a2}}$$

with

$$\frac{K_{a1}}{K_{a1}+x}+\frac{K_{a2}}{K_{a2}+x}\Rightarrow\frac{2.K_{a1}K_{a2}+K_{a1}.x+K_{a2}.x}{x^2+K_{a1}.x+K_{a2}.x+K_{a1}K_{a2}}$$

If $K_{a1} >> K_{a2}$ then $K_{a1}.x >> K_{a2}.x$ and we can consider the equations equal and derive for the electro neutrality equation:

$$\frac{K_{a1}}{K_{a1}+x}c+\frac{K_{a2}}{K_{a2}+x}c+\frac{K_w}{x}=x$$

Estimating the difference between Ka and x can help simplifying the equation even further.

Furthermore: pH = -log x.

Applying the equations derived above to the CO_2 concentrations calculated we calculate by applying that if Ka << x a valid approach if the pH is ca. 4 we can write:

$$\frac{K_{a1}}{x}c+\frac{K_{a2}}{x}c+\frac{K_w}{x}=x\Rightarrow x=\sqrt{K_{a1}.c+K_{a2}c+K_w}$$

Thus with the CO_2 concentration range in water calculated above we calculate for the pH range:

c_{low} = 0.029 mol/l ➔ pH = 3.95
c_{high} = 0.056 mol/l ➔ pH = 3.81

Verification has been done using the basic equation[*] via a numeric solution in excel employing the goal seek function. The same pH values as derived above are found.

It is possible to refine the result even further. The dissociation constant is also depending on the temperature of the solution.

Table 2: Dissociation constant (K_{1A}) of carbonic acid at various temperatures[2].

Temperature (°C)	0	5	10	15	20	25	30	35	40	45	50
$K_{1A}.10^7$	2.64	3.04	3.44	3.81	4.16	4.45	4.71	4.90	5.04	5.13	5.19

However, as can be seen in Table 2: Dissociation constant (K1A) of carbonic acid at various temperatures[2]., the pK_{a1} does not change enough to influence the pH significantly.

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[*] By transforming the basic equation:

$$c.\frac{2.K_{a1}K_{a2}+K_{a1}.x}{x^2+K_{a1}.x+K_{a1}K_{a2}}+\frac{K_w}{x}=x\Rightarrow$$

$$x^4+K_{a1}x^3+\left(K_{a1}K_{a2}-K_w-2K_{a1}K_{a2}c-K_{a1}c\right)x^2-K_{a1}K_wx-K_{a1}K_{a2}K_w=0$$

4. Effect of insoluble carbonates formation (deposits) on pH

Formation of (scale) deposits will influence the pH of solution is an indicator for a pH above 6-7. The solubility of $CaCO_3$ as a function of the pH can be described by:

$$S = [Ca^{2+}][[CO_3^{2-}] \Rightarrow [Ca^{2+}] = \sqrt{S(1 + \frac{x}{K_{a2}} + \frac{x^2}{K_{a1}K_{a2}})}$$

At lower pH's the solubility of the carbonate increases significantly as can be seen in Figure 3: Solubility of CaCO3 as a function of pH.

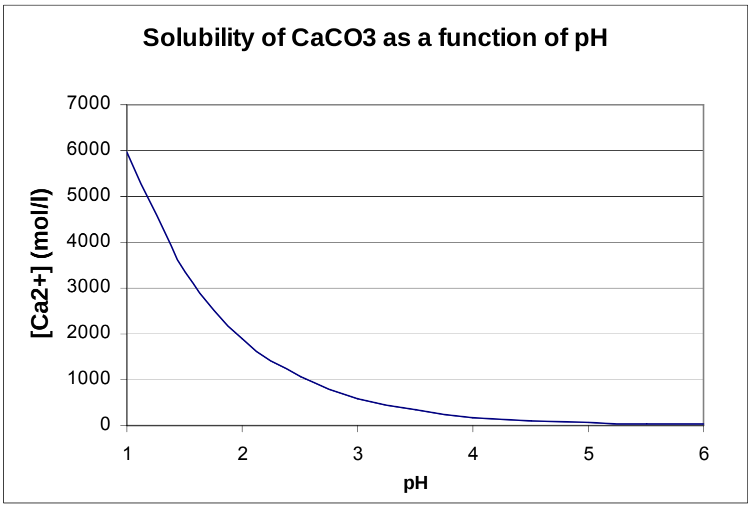

Figure 3: Solubility of $CaCO_3$ as a function of pH

Thus the absence of scaling in combination with relatively high Ca^{2+} and/or Mg^{2+} concentrations can be an indicator for a pH of the water below 6.

5. Conclusion

At the conditions under investigation, a pressure range of 80-90 bar, a temperature range of 20–35 °C and a CO_2 gas phase concentration range of 1.3-1.7 mol% the pH of the water is ca. 4.

6. References

[1] Robert C. Reid, John M. Prausnitz, and Brice E. Poling, *The Properties of Gases & Liquids*, 4 ed. Boston: McGraw-Hill, 1987.
[2] David R. Lide, *CRC Handbook of Chemistry and Physics*, 71 ed. Boca Raton, Ann Arbor, Boston: CRC Press, 1990-1991.
[3] Physical and Engineering Data, January 1978 ed. The Hague: Shell Internationale Petroleum Maatschappij BV, 1978.
[4] John J. Carroll and Alan E. Mather, "The System Carbon Dioxide-Water and the Krichevsky-Kasarnovsky Equation," Journal of Solution Chemistry, vol. 21, pp. 607-621, 1992.
[5] G. den Boef, Theoretische grondslagen van de analyse in waterige oplossingen, 4 ed. Amsterdam/Brussel: Elsevier, 1977.