The Carbonate System in Swimming Pool Water

John A. Wojtowicz
Chemcon

The carbonate system in swimming pool water is described, and formulas are given to calculate the various components of the system.

The three techniques for carbon dioxide determination found in Standard Methods (APHA 1995) are also discussed, and are compared to the more complex equations, with examples.

The carbonate system in swimming pool water consists primarily of bicarbonate ions with small concentrations of carbonate ions that are the alkaline constituents. The water also contains low concentrations of dissolved carbon dioxide (<10 ppm) and very small concentrations of carbonic acid (<0.2% of the total carbon dioxide). The combination of the alkaline and acidic components forms a buffer system that helps stabilize pH. Alkalinity (in the form of bicarbonate and carbonate ions) and calcium ions at appropriate concentrations are necessary in order to ensure saturation of swimming pool water with respect to calcium carbonate – thus avoiding etching of plaster surfaces. Etching in undersaturated water occurs by reaction of hydrogen ions with calcium carbonate on the surface of plaster, forming soluble calcium and bicarbonate ions. The hydrogen ion concentration is a function of the relative concentrations of the various components of the carbonate system. Etching is not due to any inherent aggressiveness of the water or the presence of certain aggressive species but rather to the fact that the water is not saturated with respect to calcium carbonate. Etching is avoided by maintaining a slightly positive saturation index, i.e., water that is slightly oversaturated with respect to calcium carbonate.

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Equilibria

The carbonate system in swimming pool water consists of dissolved carbon dioxide (CO_2(aq)), carbonic acid (H_2CO_3), and bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. These four species are in equilibrium with each other as shown below. Hydration of aqueous carbon dioxide forms small amounts of carbonic acid. Ionization of carbonic acid and bicarbonate ion produces small amounts of hydrogen ions (H^+). Carbon dioxide is neutral, carbonic acid is weakly acidic, and bicarbonate and carbonate are alkaline.

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$$
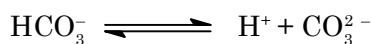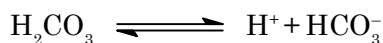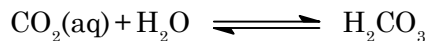
Thermodynamic Equilibrium Constants

The equilibrium expressions for the above equilibria are shown below where the braces represent activities (i.e., effective concentrations) and the K's are the thermodynamic equilibrium constants at infinite dilution (i.e., 0 ionic strength).
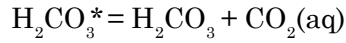
$$\{H_2CO_3\} / \{CO_2(aq)\} = K$$

$$\{H^+\} \{HCO_3^-\} / \{H_2CO_3^*\} = K_1$$

$$\{H^+\} \{CO_3^{2-}\} / \{HCO_3^-\} = K_2$$

The three K's vary with temperature and K_1 and K_2 also vary with ionic strength (i.e., total dissolved

solids or TDS). Since it is difficult to distinguish between dissolved carbon dioxide and carbonic acid by analytical means, a hypothetical species (H_2CO_3*) is used in the second equilibrium expression above to represent the total. This also reduces the number of carbonate species from four to three and simplifies calculations.

$$H_2CO_3* = H_2CO_3 + CO_2(aq)$$

The individual activities in the above equilibrium expressions can be represented as a product of an activity coefficient (γ) and a species concentration (mol/L).

$$[H_2CO_3]\gamma_{H_2CO_3} / ([CO_{2(aq)}]\gamma_{CO_{2(aq)}}) = K$$

$$[H+]\gamma_{H^+} [HCO_3^-]\gamma_{HCO_3^-} / ([H_2CO_3*]\gamma_{H_2CO_3*}) = K_1$$

$$[H^+]\gamma_{H^+} [CO_3^{2-}]\gamma_{CO_3^{2-}} / ([HCO_3^-]\gamma_{HCO_3^-}) = K_2$$

Concentration Equilibrium Constants

The activity coefficients can be combined with the thermodynamic equilibrium constants to yield concentration equilibrium constants as follows:

$$[H_2CO_3] / [CO_{2(aq)}] = K \gamma_{CO_{2(aq)}} / \gamma_{H_2CO_3} = {}^cK$$

$$[H^+][HCO_3^-] / [H_2CO_3*] = K_1 \gamma_{H_2CO_3*} / (\gamma_{H^+}\gamma_{HCO_3^-}) = {}^cK_1$$

$$[H^+][CO_3^{2-}]/[HCO_3^-] = K_2 \gamma_{HCO_3^-}/(\gamma_{H^+}\gamma_{CO_3^{2-}}) = {}^cK_2$$

Ionic Strength Correction

Activity coefficients are calculated using the Davies Approximation (Stumm and Morgan 1996) where μ is the ionic strength and z the ionic charge.

$$\text{Log } \gamma = -0.5z^2 [\sqrt{\mu} / (1 + \sqrt{\mu}) - 0.3\mu]$$

Ionic strength is calculated from ppm TDS according to the following equation:

$$\mu = 2.5 \times 10^{-5} \text{ TDS}$$

Because H_2CO_3 and $CO_2(aq)$ are not ionic species, their activity coefficients are taken as unity.

Experimental Equilibrium Constants

Temperature (degrees Kelvin) dependent equa-

tions for K_1 and K_2 (Plummer and Busenberg 1982) are as follows:

$$\text{Log } K_1 = -356.31 - 0.06092T + 21834.4/T + 126.834 \text{ Log } T - 1684915/T^2$$

$$\text{Log } K_2 = -107.887 - 0.032528T + 5151.79/T + 38.9256 \text{ Log } T - 563713.9/T^2$$

Calculated values of K, K_1 and K_2 at 25°C and 0 and 500 ppm TDS are shown in Table 1.

Equilibrium Constant	Total Dissolved Solids	
	0 ppm	500 ppm
K	1.54×10^{-3}	1.54×10^{-3}
K_1	4.44×10^{-7}	5.48×10^{-7}
K_2	4.69×10^{-11}	7.13×10^{-11}

Table 1 – Calculated Equilibrium Constants at 25°C

Concentration of Species

The total molar concentration of carbonate species is represented by the equation:

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

The molar concentrations of individual species as a function of ionization fraction (α) are given by:

$$[H_2CO_3*] = C_T\alpha_0; \quad [HCO_3^-] = C_T\alpha_1; \quad [CO_3^{2-}] = C_T\alpha_2$$

$$[H_2CO_3] = K[CO_2(aq)] \cong K[H_2CO_3*]$$

Where:

$$\alpha_0 = (1 + {}^cK_1 / [H^+] + {}^cK_1{}^cK_2 / [H^+]^2)^{-1}$$

$$\alpha_1 = ([H^+] / {}^cK_1 + 1 + {}^cK_2 / [H^+])^{-1}$$

$$\alpha_2 = ([H^+]^2 / ({}^cK_1{}^cK_2) + [H^+] / {}^cK_2 + 1)^{-1}$$

$[H^+] = 10^{-pH} / \gamma_{H^+}$ is the hydrogen ion concentration.

Ionization Fractions vs. pH

A plot of ionization fractions vs. pH is shown in Figure 1. The plot shows that as pH increases $CO_2(aq)$ and the small amount of H_2CO_3 are converted stepwise into bicarbonate and carbonate ions, the reverse being true when pH decreases. The plot also shows that at a median pH (i.e., 7.5) that $CO_2(aq)$ is only a minor constituent of pool water, corresponding to only about 6% of the total species.

Alkalinity

For pools containing carbonate, cyanurate, and borate alkalinity, total alkalinity (mol/L) is given by:

$$ALK_T = [HCO_3^-] + 2[CO_3^{2-}] + [H_2Cy^-] \\ + [B(OH)_4^-] + [OH^-] - [H^+]$$

Where: $[H_2Cy^-]$ = cyanurate ion, $[B(OH)_4^-]$ = borate ion, and $[OH^-]$ = hydroxyl ion. The presence of alkaline substances such as cyanurate and borate ions requires a correction to the typical total alkalinity determination in order to obtain the carbonate alkalinity (ALK_C) that is used in saturation index calculations (Wojtowicz 1995). In the absence of cyanurate and borate ions and neglecting the very small contributions of $[OH^-]$ and $[H^+]$:

$$ALK_C = [HCO_3^-] + 2[CO_3^{2-}] = C_T(\alpha_1 + 2\alpha_2)$$

Calculation of Species Concentrations

Using Exact Formulas – The concentrations of individual species (mg/L or ppm) can be calculated using the published temperature dependent equilibrium constants corrected for ionic strength as discussed above. Values for a given water are shown in column A of Table 2.

Using Approximate Methods – Species concentrations can also be calculated using published nomographic and numerical approximation methods (APHA 1995). The formulas for the numerical method are shown in the Appendix. Calculated values for a given water are shown in column B of Table 2. The agreement between the two calculation methods is excellent.

Analytical Determination of Species

Analytical methods are available for measuring some of the carbonate species in water such as

Species	A	B
$[HCO_3^-]$	99.6	99.7
$[CO_3^{2-}]$	0.4	0.3
$[OH^-]$	0.02	0.02
$[CO_{2(aq)}]$	6.3	6.3
$[H_2CO_3]$	0.01	0.01

A) Calculated using the exact formulas in the earlier part of this paper.

B) Calculated using the approximate formulas in APHA 1995.

Table 2 – Calculated Species Concentrations (ppm)
### Alkalinity 100 ppm, TDS 500 ppm, pH 7.5, T = 25°C

alkalinity and free carbon dioxide (APHA 1995). For example, the free carbon dioxide in pool water can be determined by titrating with standard sodium hydroxide using a pH meter or phenolphthalein indicator to detect the end point. However, the presence of significant concentrations of other acidic compounds such as cyanuric and boric acids requires a correction that will also reduce the accuracy of the determination. Similar corrections are necessary in determining carbonate alkalinity. In the presence of cyanurate alkalinity, carbonate alkalinity is obtained by correcting total alkalinity (ppm) as follows (Wojtowicz 1995):

$$ALK_C = ALK_T - \frac{1}{3} \cdot CA$$

Where CA is the measured equivalent cyanuric acid content of the water (in ppm).

Dissolution/Precipitation of Calcium Carbonate

The dissolution/precipitation of calcium carbonate can be represented by the following equilibrium reaction:

$$CaCO_3(solid) + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$$
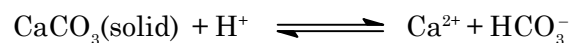
Dissolution consumes hydrogen ions whereas precipitation releases hydrogen ions. The hydrogen ion concentration is a function of the three equilibrium reactions shown on page 5. The value of the saturation index (SI) determines which process is likely to occur. A positive saturation index (SI > 0) means that the

water is oversaturated and precipitation (e.g., scaling or cloudy water formation) of calcium carbonate can occur. If the water is undersaturated (SI < 0), dissolution can occur. For saturated water, the saturation index SI = 0 and no dissolution or precipitation occurs. See Wojtowicz 1998a and 1998b for a discussion of the saturation index, and Wojtowicz 1998c for discussions on swimming pool water chemistry.

Precipitation is a function of the degree of oversaturation. Conversely, the driving force for dissolution of calcium carbonate is the degree of undersaturation, and is not due to any inherent aggressiveness of the water or the presence of certain aggressive species. For example, neither carbon dioxide nor carbonic acid *per se* can dissolve calcium carbonate. Indeed it is the hydrogen ions formed by the very small concentration of carbonic acid that is directly involved in dissolution of calcium carbonate in undersaturated water. Carbonic acid exists largely in unionized form, e.g., for the data in Table 2, the extent of ionization is only about 13%. Although very small concentrations of hydrogen ions are always present in pool water, they tend to dissolve calcium carbonate only when the water is undersaturated.

References

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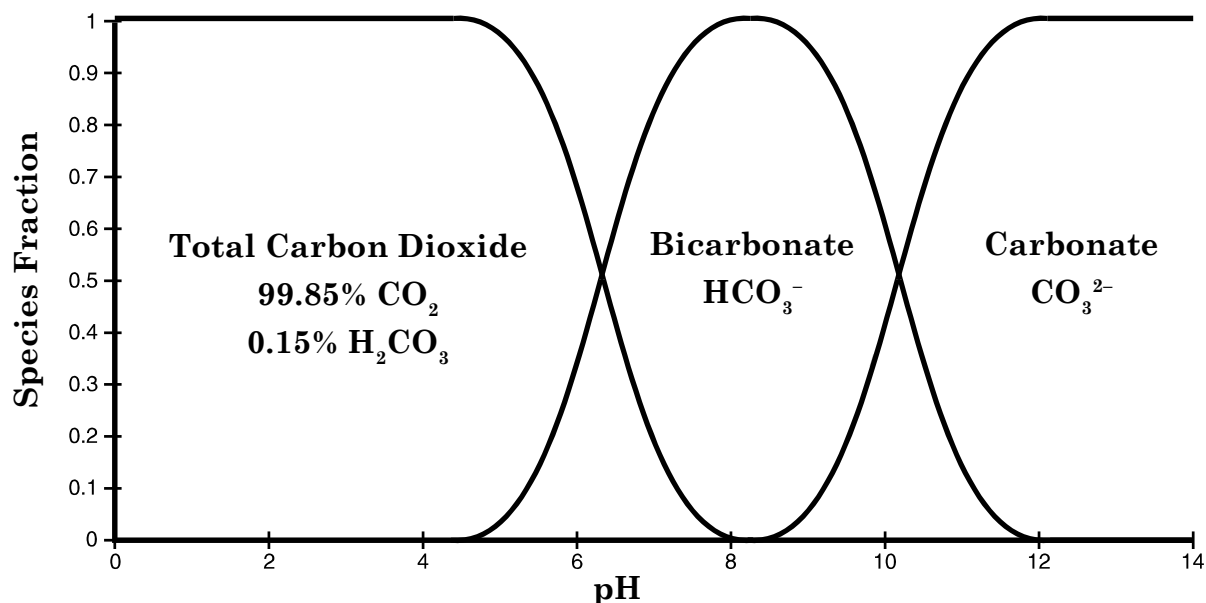
Figure 1 – Distribution of Total Carbon Dioxide, Bicarbonate, and Carbonate vs. pH

Appendix – Demonstration of a Sample Calculation

Three methods of determining free CO_2 in water are given in Standard Methods (APHA 1995), the nomographic method (4500–CO_2 B), the titrimetric method (4500–CO_2 C), and a calculation method (4500–CO_2 D). The example given in Table 2 in this article includes results using an exact formula method and when using Standard Methods 4500–CO_2 D. The water parameters in the example were: 100 ppm alkalinity, 500 ppm TDS, 7.5 pH, and 25ºC (77ºF). This assumes that all 100 ppm of the alkalinity is of the carbonate species – in other words if cyanuric, boric, or other acidic components were present, the appropriate adjustment has already been performed. Methods 4500–CO_2 B and D are illustrated below:
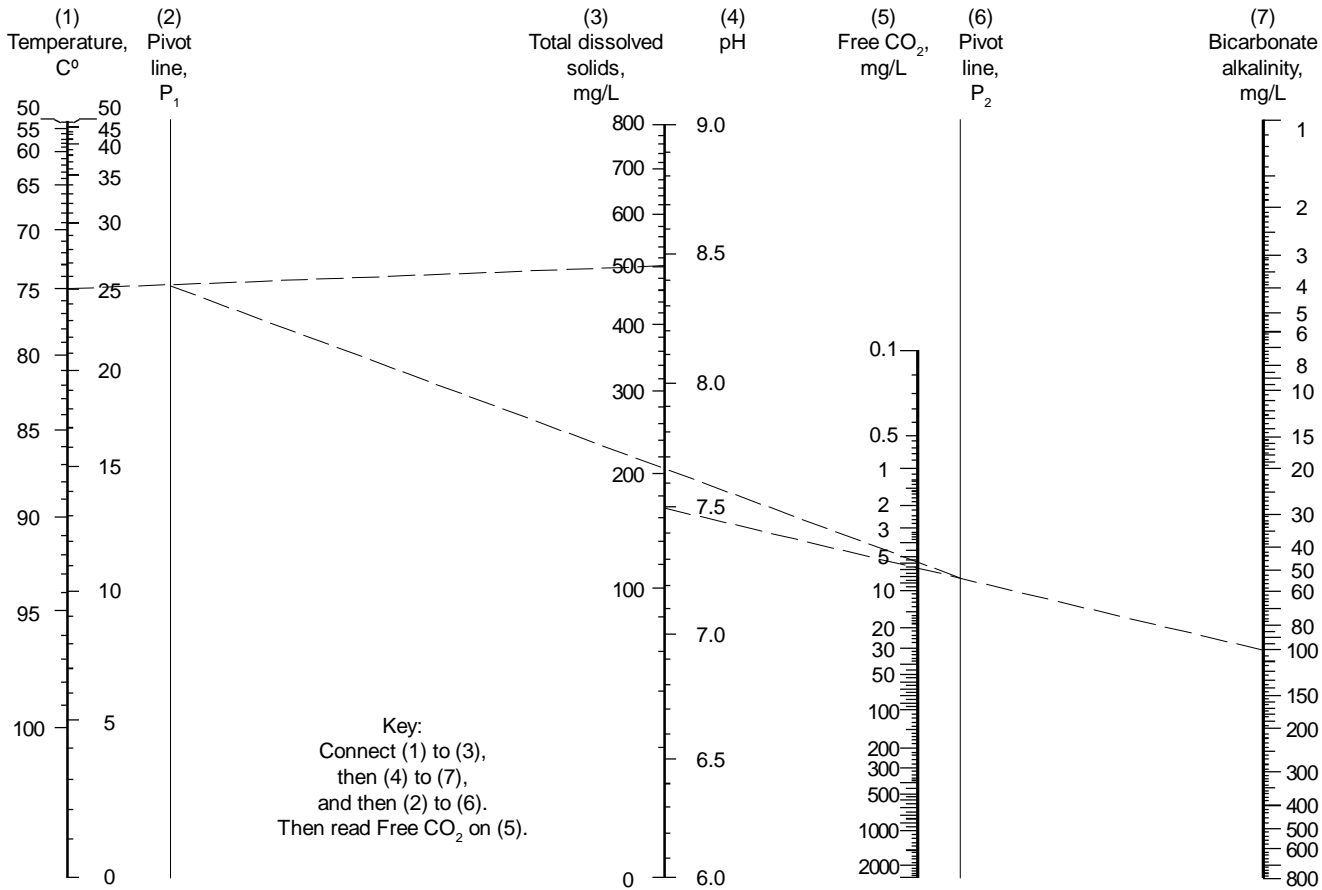
Standard Methods Figure 4500–CO_2:4

Method 4500–CO_2 B – Nomograph

To use the nomograph, align temperature (Scale 1) and total dissolved solids (Scale 3), which determines Point P_1 on Line 2; align pH (Scale 4) and bicarbonate alkalinity (Scale 7), which determines Point P_2 on Line 6; align P_1 and P_2 and read free carbon dioxide on Scale 5. In this example, temperature is 25ºC (77ºF), total dissolved solids is 500 mg/L , pH is 7.5, and bicarbonate alkalinity is 100 mg/L. Using the nomograph the free carbon dioxide content is found to be approximately 6 mg/L. (Note – for pool water application, mg/L and ppm are equivalent.)

According to Standard Methods, the precision possible using a nomograph depends on the size and range of the scales, and with practice they can be read with a precision of 1%, although the result will be biased by the accuracy of the test data (i.e., the accuracy of the pH, alkalinity, TDS, and temperature test results). Additionally, for swimming pool applications the results will be affected by any failure to completely isolate bicarbonate alkalinity.

Method 4500–CO_2 C – Titration

The titrimetric method of CO_2 determination is

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generally not acceptable for swimming pool use, both because of the order of magnitude decrease in accuracy (listed as ± 10% of the known CO_2 concentration), as well as the fact that too many common pool water components are direct interferences to the test.

Standard Methods lists the following as contributing toward "false high" readings: copper, iron, ammonia or amines, borate, and phosphate. Cyanurate will also directly interfere with the results. It is stated that those substances should not exceed 5% of the CO_2 concentration. As noted in the previous example, at a pH of 7.5 and an alkalinity of 100 ppm, the CO_2 concentration is 6.3 ppm. Five percent of that is 0.315 ppm, which is, of course, greatly exceeded by even modest amounts of cyanurate or borate. Standard Methods also lists high TDS as a contributor toward "false low" readings. Method 4500–CO_2 D – Calculation

As shown in Table 1, both the Standard Methods approximation and the exact formulas render a value of 6.3 ppm. The Standard Methods calculation is illustrated below, using the same water parameters as those used with the nomograph example above.

First, the portion of the total alkalinity that is bicarbonate alkalinity is calculated:

$$\frac{(ALK_T - 5 \cdot 10^{(pH-10)})}{(1 + 0.94 \cdot 10^{(pH-10)})} = [HCO_3^-]$$

where $[HCO_3^-]$ is the concentration of the bicarbonate alkalinity, and ALK_T is the total alkalinity. In this instance,

$$\frac{(100 - 5 \cdot 10^{-2.5})}{(1 + 0.94 \cdot 10^{-2.5})} = 99.7 \, ppm$$

Next, the carbon dioxide is determined:

$$2 \cdot [HCO_3^-] \cdot 10^{(6-pH)} = CO_2(aq)$$

or $2 \cdot 99.7 \cdot 10^{-1.5} = 6.3$ ppm

Finally, the carbonic acid can be determined:

$$K[CO_2(aq)]\frac{62}{44} = [H_2CO_3]$$

where K is $1.54 \cdot 10^{-3}$, 62 divided by 44 converts K from mol/L to ppm, and $CO_2(aq)$ and $[H_2CO_3]$ are the aqueous carbon dioxide and the carbonic acid concentrations in ppm. In this case:

$$(1.54 \cdot 10^{-3})(6.3)\frac{62}{44} = 0.01 \, ppm \, carbonic \, acid$$