

Marine Water pH Control

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pH is generally understood to be an expression of acidity or the hydrogen ion (H^+) concentration in water. The value is a negative logarithm, which means that acidity increases as the value decreases and that each unit change reflects a 10-fold change. Although not totally correct, this concept serves us well and is not difficult to comprehend.

In considering pH and pH control in the marine environment, however, the inadequacies of this concept have caused some fundamental misreasoning.

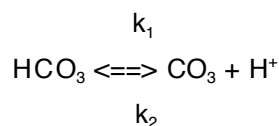
pH is what the pH meter reads: a negative logarithmic expression of the hydronium ion concentration (or hydrogen ion activity). The hydronium ion (H_3O^+) is ionized water. Ionized water exists in equilibrium with unionized or free water: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$. One molecule of water acts as an acid or proton donor and another as a base or proton acceptor. The presence of negative ions shifts the equilibrium in the direction of free water, while the presence of positive ions favors ionized water. In freshwater, there are relatively few ions to complicate the picture and those present are counterbalanced, so that behavior approaches the ideal. This is not the case in marine water.

The astute reader has noticed a striking similarity between this equilibrium and that of ionized ammonia and free ammonia: $H_2O + NH_3^+ \rightleftharpoons NH_4^+ + OH^-$. The phenomenon, of course, is fundamentally the same. Again, water acts as a proton donor or acid, while ammonia acts as a proton acceptor or base. Before proceeding, a look at the notion of equilibrium is in order.

Equilibrium does not mean that the components in equilibrium are present in equal concentration. It means that the interconversion between the two takes place at the same rate. The concept of chemical equilibrium is probably best understood by a physical analogy:

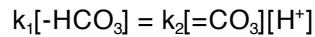
Visualize two containers of water connected to each other by a siphon tube. The containers may be of different sizes or may be at different levels, and thus contain different amounts of water, but the water levels in each will be the same by virtue of the siphon tube: the containers are at equilibrium. If we lower one of the containers or increase its size, the water level will drop in that container, but the siphon tube will rapidly readjust the water levels to restore equilibrium. We have shifted the amount of water from one compartment to another and have established a new equilibrium.

A buffer is a system of chemical equilibrium that has the effect of stabilizing pH. It is an equilibrium mixture of ionized or relatively dissociated species and free or relatively undissociated species. As an example, bicarbonate exists as a relatively undissociated species, the bicarbonate ion and the relatively dissociated species, carbonate:



k_1 represents the rate constant for the dissociation of bicarbonates to carbonates and hydrogen ions (and, consequently, hydronium ions). k_2 represents the rate constant for the association of carbonates and hydrogen ions. The rate of dissociation is equal to the rate constant times the concentration of the species, or the rate of dissociation of bicarbonate is equal to $k_1[HCO_3]$ and the rate of association is equal to $k_2[CO_3][H^+]$. Since, by definition, under

equilibrium condition, the rates are equal



it is possible to derive a new constant $K = k_1/k_2$ and express the acidity as

$$[\text{H}^+] = K([\text{HCO}_3]/[=\text{CO}_3])$$

Just as pH is defined as the $-\log(\text{H}^+)$, that is, the negative log of the hydrogen ion activity, pK is defined as the $-\log K$.

The relationship of pH to pK is expressed by the equation

$$\text{pH} = \text{pK} + \log([\text{dissociated}]/[\text{undissociated}]) - \log a_{\text{H}^+}$$

This very important equation expresses the reality that when the concentration of dissociated species is equal to the concentration of undissociated species the pH is equal to the pK, modified by the activity coefficient a_{H^+} . The value of the activity coefficient and, consequently, the pK is very much influenced by the kind and concentration of other ions present in solution.

When pH is equal to pK, the buffer is at optimum efficiency. This is particularly important in the aquarium where buffers are actually very dilute. Buffer efficiency is determined by pK alone, while buffer capacity is determined by concentration alone. The greater the concentration of buffer components and the closer pH is to pK, the greater is the quantity of acid or base the buffer system can handle with relatively little change in pH. Under aquarium conditions, any change in pK will change the pH.

Marine water is buffered principally with a carbon dioxide-bicarbonate-carbonate equilibrium. Borate is a secondary buffer. A pure bicarbonate-carbonate buffer has a pK of 9.2. Positive ions will shift the pK to a lower value, while negative ions will shift it to a higher value. While all ions have a counter ion, the complex mixture of ions in sea water can produce effects difficult to predict, because most ions do not compete equally for counterions. The influence of divalent ions is generally more pronounced than that of monovalent ions. Depending on the ion mix, the influence of calcium, magnesium, and sulfate can be significant.

Contrary to the prevalent assumptions, we have accumulated extensive data and experience that indicates that marine aquarium pH is better and more easily controlled with inert substrates such as foam, quartz, coated dolomite, oyster shell, than with dissolving substrates, most notably, crushed coral.

Ten 40 gallon tanks filtered with crushed coral all exhibited the same symptom of rapid pH drop from an initial 8.4 - 8.6 to 7.5 - 7.6 within a few days. With no intervention, and no life to support, three of the tanks ultimately fell to 7.4 after one month and were stable at that pH thereafter. One tank, with no intervention, but with a small biological load, behaved similarly. Three other pairs, with and without a biological load, were treated, as required, with sodium carbonate, sodium bicarbonate, and Marine Buffer (SeaChem). All three were effective in raising pH to 8.3, although sodium carbonate required caution not to overshoot. Neither sodium carbonate or bicarbonate were capable of maintaining the pH for more than two days. Marine Buffer maintained the pH for several weeks. The ability of Marine Buffer to maintain pH improved with use, while neither carbonate or bicarbonate improved with continued use. A survey of other ions indicated that, regardless of biological load, calcium concentrations increased markedly and magnesium decreased, chlorides were constant, sulfates decreased, carbonates increased. In the tanks treated with Marine Buffer, calcium increased, but much less than in the other tanks, magnesium increased, chlorides and sulfates were constant, carbonates increased.

Ten other tanks were filtered through dolomite, crushed oyster shell, quartz, and foam. All of these had a biological

load. Both dolomite and crushed oyster shell showed a minor pH drop to 7.9 - 8.0. after a few days, then dropped gradually to 7.6 over a 30 day period. Carbonates raised the pH and were able to maintain it for about a week. Marine Buffer maintained the pH for close to a month. Compared to the crushed coral tanks, all other ions were fairly stable. Best pH stability was secured with the other inert substrates. Even untreated, these tanks maintained a pH 7.9 -8.0 for several weeks before intervention with carbonates or Marine Buffer became necessary. Carbonates maintained a pH of 7.9 - 8.0 for a few weeks. Marine Buffer maintained a pH of 8.3 for over a month.

It is evident from our experience and the understanding of buffers described above that the addition of calcium ions in the form of carbonates (lime, crushed coral) will ultimately lead to a pH drop, and ultimately, to a buffer at pH 7.6. This experience and the consequent conclusions have been confirmed by several hobbyists and professional aquarists. For the same reasons, the use of bicarbonate or carbonate to raise pH only increases the capacity of the buffer and temporarily raises pH, but does not significantly raise the pK of the buffer. To buffer at pH 8.3, it is essential to have the proper balance of counterions to control the pK of the buffer. It is not sufficient to merely increase the capacity of the buffer. This is best accomplished by scientifically formulating the salt mix or adding a properly formulated buffer to the aquarium so as to produce a buffer system with a pK of 8.3. Further, it should be self-evident that this is more easily maintained if the aquarium substrate is inert and does not release ions into the water that will cause a drop of the pK.