Understanding the General Chemistry of the Planted Aquarium

Gregory Morin, Ph.D

INTRODUCTION

When it comes to capturing a little bit of nature in our homes, we aquarium keepers have managed to pick the most difficult environment to reproduce. The difficulty arises from the numerous chemical parameters that must be controlled. These include dissolved ions, dissolved gases, pH, and waste. In an open, aquatic system these parameters are naturally controlled through a complex system of self-regulating feedback based control mechanisms. However, in a closed aquatic system the self regulation exists only very tenuously at best and can be easily overwhelmed if the system is not adequately maintained.   Proper maintenance requires our intervention where Nature normally would step in. This maintenance involves the application of simple chemical principles. Although one can maintain a tank without understanding the principles being applied, a basic understanding can help to take some of the mystery out of what we do and why we do it. Additionally, the more one understands, the more likely it is one will be able to avoid a disaster or achieve a greater level of success.
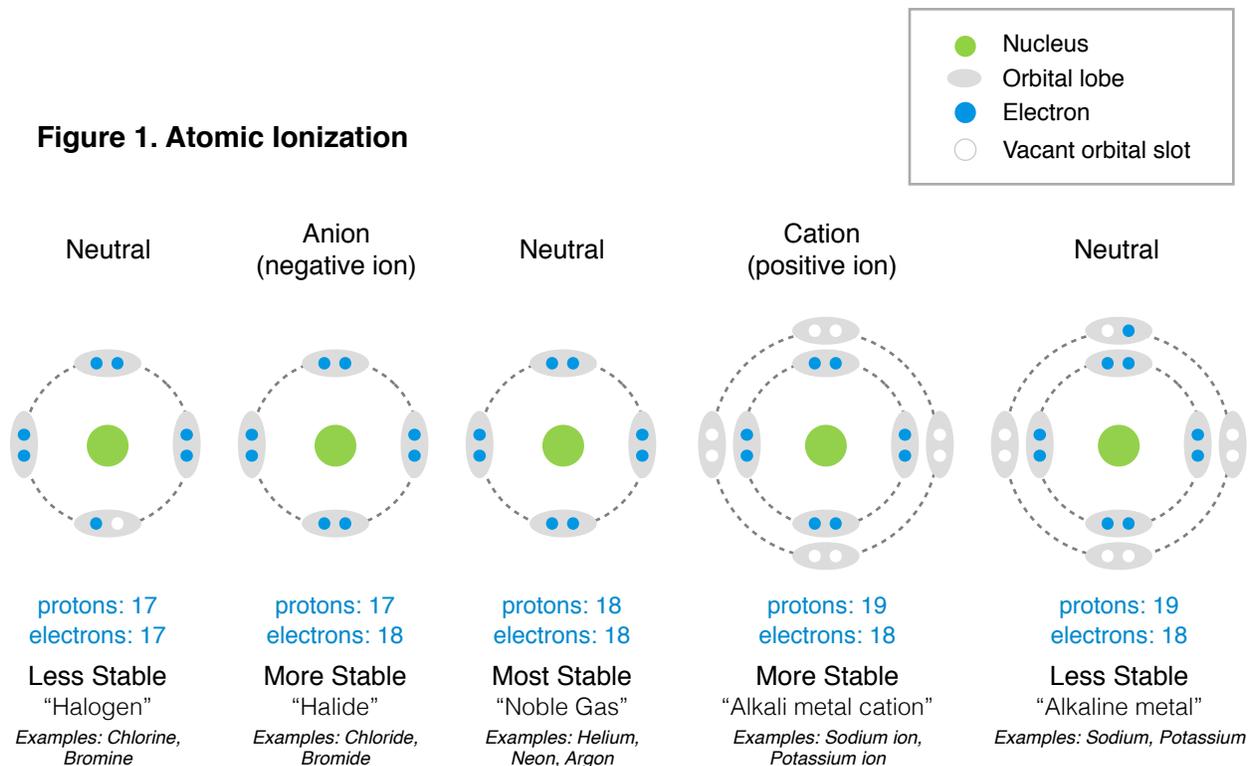
ATOMS

Before proceeding with any discussion of the chemistry that occurs in an aquarium it is necessary to briefly touch upon some rudimentary general chemistry. Without this basic knowledge, any further discussions would be of little benefit. All matter (living organisms, soil, air, water, asteroids, stars, etc.) are composed of atoms. An atom is the smallest unit of matter that still retains the unique properties of its element. An element is matter that is composed of only one type of atom.   Examples of elements include carbon, oxygen, nitrogen, and iron.   Atoms themselves are composed of even smaller parts: electrons, protons, and neutrons.   Protons carry a positive charge, electrons a negative charge, and neutrons are neutral. Every atom is composed of these three basic components (only hydrogen lacks a neutron). For example, a proton in an atom of gold is exactly the same as a proton in an atom of oxygen. What distinguishes elements is the number of protons found in their respective atoms. For example, oxygen has 8 protons, while gold has 79. Each atom houses its protons at its core, along with a certain number of neutrons. This core is called the nucleus of the atom. In a neutral atom the nucleus is surrounded by the same number of electrons as protons. This can be simplistically visualized as equivalent to planets orbiting a star although a more accurate picture would be akin to bees buzzing about a hive: random, unpredictable movement in a spherical swarm.

IONIZATION OF ATOMS

Some atoms are more stable than others. This stability is related to the number and location of electrons orbiting the nucleus.   Some atoms try to be "like" their more stable cousins by giving up or gaining electrons so that their configuration of electrons is identical to that of their nearest most stable cousin.

In Figure 1 (next page) we see that the central configuration is the most stable and is represented by a nucleus surrounded by an orbital shell containing four pairs of electrons. There are multiple shells but only the outermost one is shown for clarity. These stable elements are commonly called "noble gases".

Figure 1. Atomic Ionization

Neutral	Anion (negative ion)	Neutral	Cation (positive ion)	Neutral
protons: 17 electrons: 17	protons: 17 electrons: 18	protons: 18 electrons: 18	protons: 19 electrons: 18	protons: 19 electrons: 18
Less Stable "Halogen"	More Stable "Halide"	Most Stable "Noble Gas"	More Stable "Alkali metal cation"	Less Stable "Alkaline metal"
Examples: Chlorine, Bromine	*Examples: Chloride, Bromide*	*Examples: Helium, Neon, Argon*	*Examples: Sodium ion, Potassium ion*	*Examples: Sodium, Potassium*

Legend: Nucleus, Orbital lobe, Electron, Vacant orbital slot

They are so stable that they do not normally react with any other elements in any way. In Figure 1 (left side) we see that the halogens (elements with one less proton in their nucleus than their nearest noble gas neighbor) will gain an electron so their electron configuration is the same as their nearest noble gas neighbor. Because they have an extra electron they are negatively charged and called negative ions (anions). An atom is in a neutral state when the number of electrons is the same as the number of protons. Likewise (Figure 1), an element with one more proton than its nearest noble gas neighbor (alkali metal) will give up an electron so that its electron configuration is the same as its nearest noble gas neighbor (the outer shell is empty and can be ignored here). Because it is lacking an electron it has a positive charge and is called a positive ion (cation).

MOLECULES

When atoms combine they form larger structures called molecules. Each molecule of a substance is identical to every other molecule of that substance. The atoms in a molecule are held together by an energetic association known as a bond. A bond can most simply be characterized in terms of its strength. The three basic bond types (strongest first) are covalent, ionic, and coordinate (or dative). Covalent bonds are difficult to break and cannot be broken by dissolving in water. Ionic bonds are much weaker and are typically easily broken in water solution. Coordinate bonds are the weakest and actually are not a true physical bond but rather more of a strong association based on opposite charges.

In general, if an element is bonded to a halogen (fluorine, chlorine, bromine, iodine) it has an ionic bond. If an element is bonded to carbon, nitrogen, or phosphorous it has a covalent bond.

Molecules can have a mixture of different bonds. Some parts of a molecule may be held together by covalent bonds while other parts are held together by ionic bonds. For example, sodium bicarbonate has three oxygen atoms bonded to a central carbon atom (see Figure 9). Two of the oxygens are ionically bonded to hydrogen ion and sodium ion respectively. Ionic bonds are considered to be highly polar. This means that there are predominantly positive and negative areas to the bond (similar to the poles of a magnet). These "opposites" attract each other quite strongly, forming the ionic bond.

In the presence of a solvent that possesses some polar character (such as water) these ionic bonds will break, releasing the individual components which are then stabilized by the overwhelming number of polar solvent molecules. This helps us to understand why certain compounds dissolve in water and why they dissolve in the manner that they do (e.g. sodium bicarbonate yields sodium cation, hydrogen cation, and carbonate anion, but no carbon or oxygen ions).

ACIDS & BASES

Other than salts (such as table salt, sodium chloride), the next most well known example of ionic based bonding is found in acids and bases. But first, what is an acid? What is a base? Acids are defined as substances that are capable of donating a hydrogen ion, and bases as substances capable of accepting a hydrogen ion. Acids and bases can be either strong or weak. A strong acid (of which hydrochloric acid is a well known example) will be completely ionized when added to water. There will be no hydrochloric acid molecules left in the water, only chlorine ions (chloride) and hydrogen ions. The latter part of the last statement is a slight over simplification. Free hydrogen ion (H^+) attaches itself to a water molecule.

Figure 2.Strong acid solvation

| hydrochloric acid | water H_2O | hydronium ion H_3O^+ | chlorine ion (chloride) |
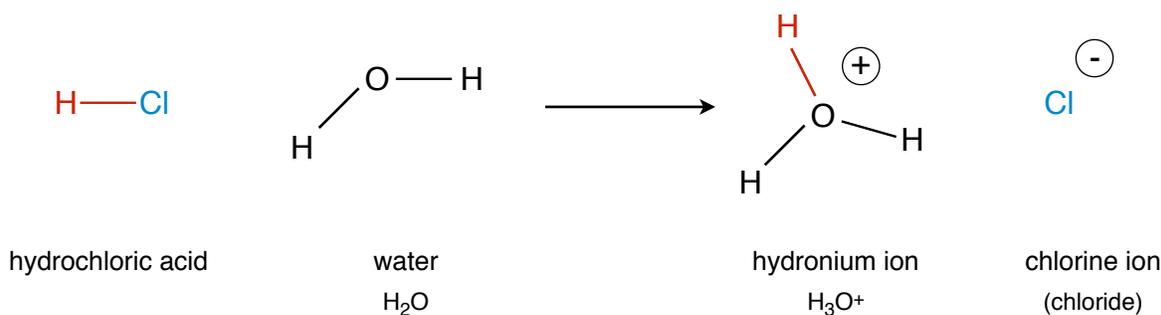
As seen in Figure 2, the actual form of hydrogen ions is that of the hydronium (H_3O^+) ion.

pH

When we measure pH we are actually measuring the concentration of the hydronium ion in the water(power of Hydronium, pH). Because the concentration of hydrogen ion is typically quite small, it is easier to refer to pH in terms of the negative logarithm of the concentration rather than the concentration itself (pH 7 is a little easier to recite than pH 0.0000001). This also explains why high acidity is expressed by low pH values (an otherwise counter intuitive convention). A weak acid or base is one that does not completely ionize when dissolved in water.

A well known example of a weak base is ammonia. This example can also be used to highlight the central duality between acids and bases (Figure 3).

Figure 3. Ammonia Equilibrium
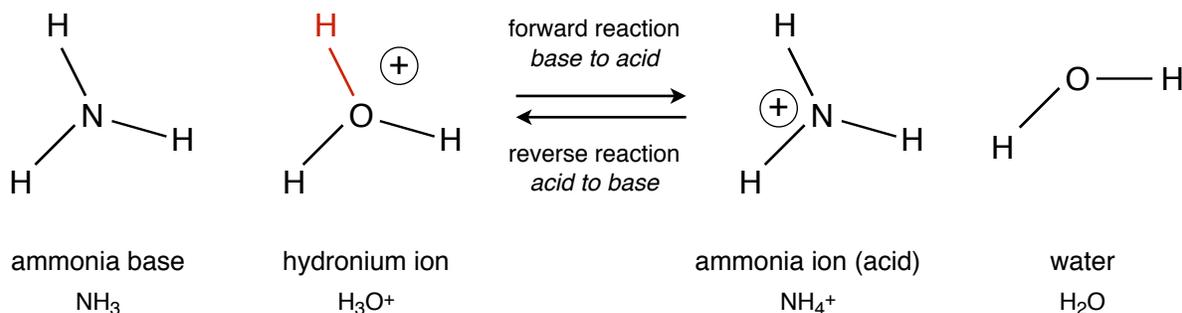
When ammonia (NH_3), a base, accepts a hydrogen ion, it produces NH_4^+, the conjugate acid of NH_3. When NH_4^+, an acid, releases a hydrogen ion, it forms the conjugate base, NH_3. The transformation of one into the other and back again results in an equilibrium. The relative balance between the two forms is described by an equilibrium constant, K. This balance is determined by the ratio of the product of the concentrations of the chemical products to the product of the concentrations of the chemical reactants (Figure 4).

Figure 4. Equilibrium Constant
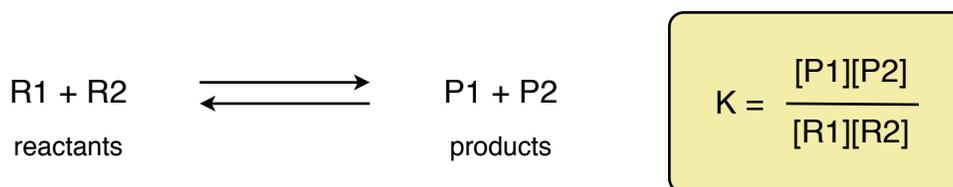
R1 and R2 are two hypothetical reactants. P1 and P2 are likewise two hypothetical products.
K is the equilibrium constant for this reaction

This constant is a function of the relative stability of the products and reactants in the selected solvent (typically water). The pH of the solvent can influence the relative position of the equilibrium but not the equilibrium constant itself. In other words, the equilibrium constant, K, does not change. The reason pH can influence the position of the equilibrium is explained by LeChatelier's principle, which says: "If a system at equilibrium is disturbed by a change in temperature, pressure, or the concentration of one of the components, the system will tend to shift its equilibrium position so as to counteract the effect of the disturbance."

Figure 5. LeChâtelier's Principle

$$NH_4^+ \rightleftharpoons NH_3 \quad\quad H^+$$

Concentration at	ammonium ion	ammonia	hydrogen ion	Products/Reactant ratio
at equilibrium:	4.75	7.00	7	9.25
upon addition:	4.75	7.00	6	8.25
at re equilibration:	4.74	7.99	6	9.25

*All values expressed as the negative logarithm (i.e –log[value])*

This principle applies to any process involving some type of equilibrium. In Figure 5 we have simplified the ammonia/ammonium equilibrium in terms of only those components that see an appreciable change in their concentration. The concentration of water is basically constant, thus it can be incorporated into the equilibrium constant, K, to yield a new value, K_a (the acid dissociation constant). The negative log of K_a is the pK_a, which for ammonium is 9.25. However, the main purpose of Figure 5 is to illustrate LeChatelier's principle by showing that lowering the pH (increasing the hydrogen ion concentration) results in the ammonia level dropping and the ammonium level rising. These changes occur in order to reestablish the equilibrium and return the ratio of product and reactant to its equilibrium value.

BUFFERS

A buffer consists of two parts (i) a weak acid or base and (ii) a salt of that weak acid or base. The equilibrium constant for the weak acid or base dictates what pH the buffer will most strongly maintain. The salt of the weak acid or base allows us to set the desired ratio between the conjugate acid and conjugate base so that the buffer will start out at the desired pH. For example, a bicarbonate based buffer employs a weak acid (carbonic acid) and a salt of that acid (sodium bicarbonate). To determine the resultant pH we use the Henderson-Hasselbalch equation (Figure 6, next page) which helps clarify how the ratio of acid and base affect the pH. In this equation we see that when the acid and base components are in equal concentrations the pH is equal to the pK_a of the acid (6.35 for carbonic acid). Since the relationship between the acid and base ratio is expressed logarithmically, otherwise large shifts in the amount of acid or base produce very small changes in the final pH.

However, once one exceeds more than a 5-fold excess of one component over the other the pH change becomes large. If the absolute amount of the buffer components is large, then the capacity for the buffer to resist a change in pH is large also.

Figure 6. Henderson-Hasselbalch Equation

$$pH = pK_a + \log \frac{[base]}{[acid]}$$

base/acid ratio
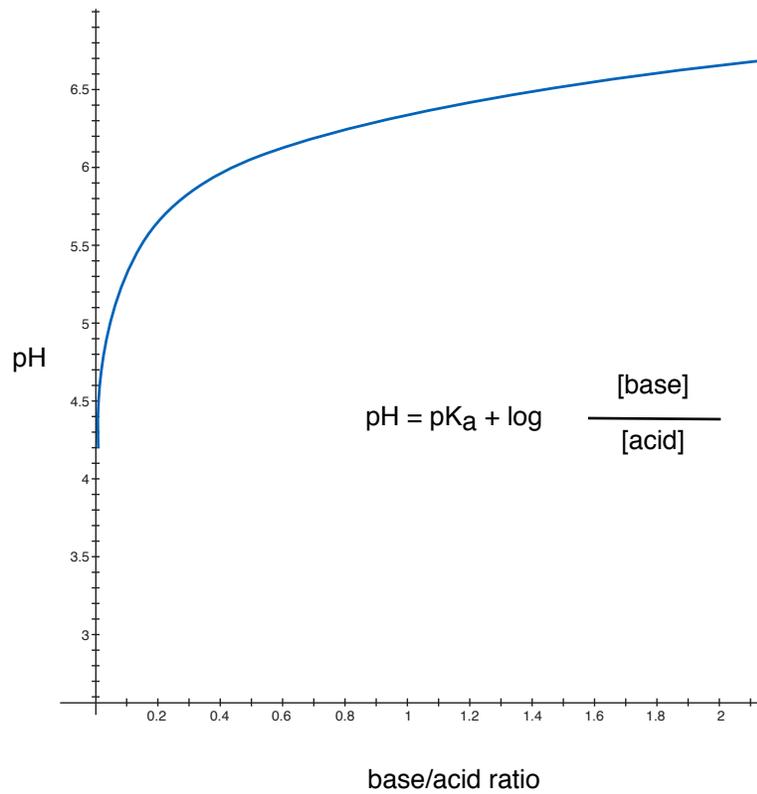
This graph shows a plot of Henderson-Hasselbalch equation for H_2CO_3/HCO_3^- with pk_a value of 6.3.
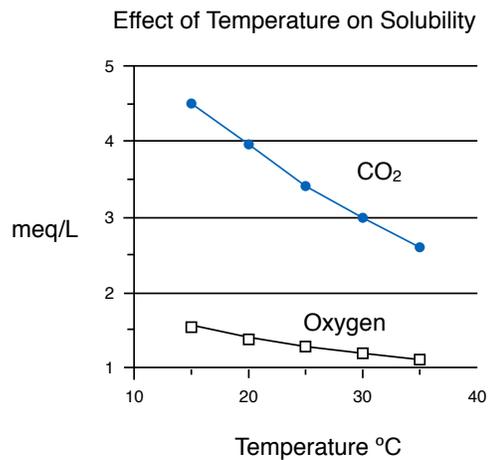*The equation graphed then is y=6.35 = log x*

GAS LAWS

Henry's law (Figure 7) illustrates the relationship between the pressure of a gas above a solvent and the concentration of the gas in that solvent. As the pressure of the gas (P_g) increases, so does the concentration of the gas (C_g) in the solvent (k is a proportionality constant).

Figure 7. Gas Laws

Effect of Temperature on Solubility

Henry's Law

$$C_g = kP_g$$

Temperature-Gas Solubility Relationship

$gas_{free} \longrightarrow\hspace{-1.5em}\longleftarrow gas_{dissolved} + heat$


Temperature °C

As temperature increases, solubility decreases for gases because dissolving gas into water is an exothermic process (gives off heat). Putting heat into the system will result in an increase of free gas as LeChatelier requires. At elevated temperatures the levels of dissolved CO_2 and O_2 (oxygen) decrease (see Figure 7: CO_2 concentration is given assuming a 10% CO_2 atmosphere which is the upper limit found on most CO_2/HCO_3^- charts, O_2 is given assuming 100% O_2 atmosphere).

CO_2 and KH

The use of a carbonate buffer can be quite tricky because of one unique aspect that is not found in other buffer systems. Normally one gains or loses the acid component in a buffer with a change in pH. But with a carbonate buffer one can also gain or lose the acid component (carbonic acid) with a change in CO_2 concentration. CO_2 concentration is affected by temperature, aeration, or CO_2 pressure in the gas over the water. This brings us back to LeChatelier's principle. A decrease of CO_2 in the water will result in a decrease of carbonic acid in the water (see Figure 8).

Figure 8. The Carbonate Buffer Equilibrium

carbon dioxide   carboic acid   bicarbonate   carbonate
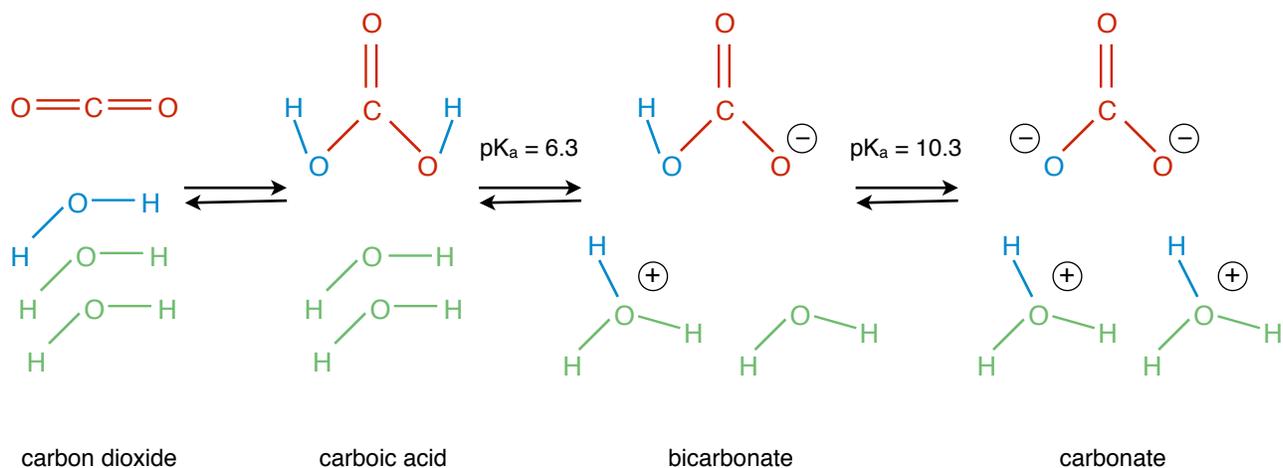
The carbonic acid concentration decreases so as to bring the system back into equilibrium with the new lower level of CO_2. When the carbonic acid level drops, the bicarbonate level drops as well which in turn yields a higher pH (see Figure 9, bicarbonate: dropping levels of bicarbonate necessarily produce a drop in hydronium ion). Likewise, an increase in CO_2 will result in an increase in carbonic acid, followed by an increase in bicarbonate and its concomitant hydronium ion, which results in a pH decrease.

ALKALINITY and KH

There is much confusion over these terms. We will not delve into the unfortunate reasons for this right now, but rather will try to simply clear the air by defining and clarifying these terms:

Alkalinity: a measure of the ability of water to resist a decrease in pH upon the addition of an acid. The greater the number the greater the alkalinity (within a particular scale system). Alkalinity can be provided by any number of compounds (carbonate, bicarbonate, borate, phosphate, hydroxide). Thus a measure of alkalinity does not necessarily indicate the presence of any one of the above compounds.

KH:carbonate hardness. A measure of the amount of carbonate/bicarbonate in a given volume of water. In general this is typically the same as the alkalinity value, but it is not necessarily always so.

Temporary hardness: another name for KH. It is temporary because (as we read above) changes in CO_2 concentration and acid levels can rapidly affect this value. This is in contrast to GH (general hardness) which does not appreciably change in the short term.

General Hardness: a measure of the calcium and magnesium concentration.

SUMMARY

To fully explain how CO_2 and KH work in a planted aquarium you must understand the other topics here too. Atoms make up the bicarbonate molecule, which is held together by covalent and ionic bonds. When added to water the molecule will dissolve forming anions and cations and will set up an equilibrium between the carbonate, bicarbonate and carbonic acid forms. Changes in either pH, CO_2, bicarbonate or carbonate will influence the concentration of the other three. These changes occur because of LeChatelier's principle.

In a planted aquarium employing a properly set up CO_2 injection system the KH and pH should remain stable because one adds only as much CO_2 as the plants need, thereby maintaining a constant level of CO_2. In practice this is what you get when you use a CO_2 injection system with a pH feedback metering system.

Although you rarely have pH/KH problems when using this system, there does still exist a chemical route by which KH and pH can drop that cannot be remedied by a CO_2 system. This possibility exists because planted aquaria produce numerous acidifying organic compounds (e.g. tannic, humic, and uric acids) that will react with the KH (bicarbonate/carbonate) present. This reaction converts bicarbonate into carbonic acid. The carbonic acid produces CO_2 that can (i) be utilized, (ii) be gassed off, or (iii) re equilibrate (however the amount of bicarbonate produced is a tiny fraction of what was initially consumed). One would be alerted to this situation by a rapid drop in pH (which occurs when the bicarbonate concentration falls below the CO_2 concentration). Once this occurs it is chemically impossible to restore this lost KH by maintaining or increasing the level of CO_2 injection.

This relationship becomes evident when we look at the equilibrium equation illustrated in Figure 4. For H_2CO_3 & HCO_3^- the K value is 0.000000447. When we consider that the bicarbonate concentration is in the numerator and carbonic acid (CO_2) is in the denominator in this ratio it becomes clear that no matter how large the denominator becomes, the numerator will always be much, much smaller.

However, this drastic loss of KH is not something that commonly occurs because most people perform a water change well before that situation might arise. The water change water either already has a sufficient KH or can be brought to the appropriate level with the use of a bicarbonate based buffer. Although this is rare, it is important to be aware of lest anyone become complacent and forgo water changes for several months. How rapidly this process occurs is related to the overall cleanliness of the system (i.e. effective waste removal) and the initial KH.

In a well planted tank without CO_2 injection the plants will use the CO_2 available, causing the carbonates present to re equilibrate thereby producing more CO_2. The acidifying agents mentioned above will also tend to drive the bicarbonate equilibrium to produce more CO_2. In this type of setup the presence of acidifying agents can have a beneficial effect; it helps to maintain a higher level of CO_2 than would be present if utilization were the only driving force for the formation of additional CO_2. With this system one must actively maintain the KH by periodically adding bicarbonate based buffer. The plants are in essence 'eating' the buffer.

The plants' use of CO_2 and the presence of acidifying agents in the water drive the bicarbonate equilibrium to maintain a constant level of CO_2. In most cases the amount of CO_2 produced is adequate for moderate to good levels of growth, however if the plants are capable of consuming CO_2 faster than re equilibration can produce it, then the re equilibration step will become the limiting factor in plant growth (assuming all other nutrients are at levels sufficient to not limit growth). The bicarbonate based buffering system maintains KH and pH because of LeChatelier's principle. Without an understanding of this basic chemical principle we would be unable to explain how one of the most basic systems in a planted aquarium functions.

REFERENCES

Lide, D.R. (Ed). 1998. *Handbook of Chemistry and Physics*, 79th Edition, CRC Press