The chemistry of swimming pools

Pool chemistry is the application of chemistry to maintain safe and clean water (Hann, 1997). This is achieved by regulating numerous factors which include: the pH, the quantity of disinfectant and the buffers used to resist pH changes. The normal pH range of a swimming pool needs to be between 7. 2 and 8. 0, although a range between 7. 2 and 7. 8 is more practical as some disinfectants such as chlorine are most effective for this range (Hann, 1997).

The Importance of pH

The pH scale (see figure 1) is a measure of the concentration of hydrogen ions (H+) in a solution and is a logarithmic scale based on 10 (Zumdahl, 2007). Furthermore, it is represented by the equation: pH = -log[H+] (Zumdahl, 2007), and since the scale is logarithmic, this means that a pH increase of one value represents a H + concentration increase of tenfold. The pH scale ranges from one, which is very acidic, to fourteen which is very alkaline. A value of seven is neutral, meaning that a solution is neither acidic nor basic (Hann, 1997).

The pH scale

(Environment Canada, 1992)

A strong acid dissociates completely in water to produce H+ ions in the form of H3O+ (hydronium ion), whereas a weak acid does not dissociate completely, causing a lower H+ concentration to form (Zumdahl, 2007). Since an acid dissociates in water to produce H+ ions it is known as an H+ donor and a good example of this is the strong hydrochloric acid (HCl). This acid easily dissociates in water to form H+ and the following equation represents this dissociation.

HCl(aq) + H2O(l) ® H3O+(aq) + Cl-(aq)

Because HCl is easily dissociated, it means that equilibrium lies far to the right, favouring the products. On the contrary, a weak acid does not easily dissociate in water, meaning that a reaction involving a weak acid would not favour products or reactants. In contrast to an acid, a base dissociates in water to form OH- and is known as an H+ acceptor.

The role of acids and bases for the maintenance of the pH of pool water is important for a number of reasons. A pH that is too high or low (above 8 or below 7. 2) will cause irritation to the skin (Gothard, 2006). As well as this, disinfectants such as bromine and chlorine require an optimum pH between 7. 2 and 7. 6 in order to function most efficiently (Hann, 1997). Thus, an increase or decrease in pH will cause these disinfectants to work less efficiently.

Another reason for the regulation of the pH balance is to prevent the formation of scale or water hardness deposits. These deposits are usually composed of magnesium and calcium which can become damaging to the functioning of a pool as it affects the filter system, heater and the piping (Hann, 1997).

Maintenance of the pH levels

Factors such as, the removal or addition of pool water; waste from swimmers such as urine; and the addition of chemicals, affect the pH of the water. In order to have a pH level that is desirable, specific chemicals need to be added to the water, although it is also possible to reach a desired pH balance by adding extra water to the pool (Hann, 1997). By adding additional water this will cause the pH concentration to lower, which helps to balance the pH. However, it is not always possible to do this as different factors affect the pH, and so pool chemicals are needed.

Two main chemicals are used to lower the pH of pool water: sodium bisulfate and muriatic acid (hydrochloric acid). These chemicals both have a low pH which means that they act as a “ pH reducer”. A decrease in pH occurs because the chemicals react in the water to produce more hydrogen ions, hence increasing the acidity. The choice of which chemical to use depends on the size of a pool. Sodium bisulfate is usually used for small pools (about 190 000 litres) as it is less acidic than muriatic acid, thus a safer alternative (Hann, 1997). On the other hand, muriatic acid is used for larger pools to reduce the pH because it is a more acidic. Furthermore, to raise the pH of pool water, sodium carbonate is most commonly used (Perkins, 2000). It is known as a “ pH increaser” because it produces hydroxyl ions (OH-) which increases the pH of the pool water. Chlorine also has an effect on the pH of water; however, it is used more commonly for disinfection purposes.

Chlorine for Disinfection of Pool Water

A safe and clean pool requires the use of a disinfectant to stop the spread of transmittable diseases (Hann, 1997). The most common disinfectants used are chlorine-based products as chlorine is relatively inexpensive and is very effective in killing bacteria and other harmful organisms (Perkins, 2000). Chlorine gas (Cl2) is never used on its own for disinfecting pool water because it is very toxic, and so would pose many risks. Therefore, compounds containing chlorine are used instead and there are three main types: Calcium hypochlorite [Ca(OCl)2], sodium hypochlorite (NaOCl) and chlorinated isocyanurate.

When these compounds are added to the water a reaction occurs, forming a chemical called hypochlorous acid (HOCl) which is an oxidising agent and hydrochloric acid (HCl). Since hydrochloric acid is formed, this will mean that the pH of the pool water decreases slightly.

Cl2 + H2O ® HOCl + HCl

The hypochlorous acid kills the bacteria in the water by oxidation and the HOCl can easily become dissociated to from hydrogen ions (H+) and hypochlorate ions (ClO)-.

HOCl â†” H+ + ClO-

Both the hypochlorous acid and the hypochlorite ions are considered as " free chlorine", which is the chemical species responsible for killing bacteria in the water; however, the hypochlorous acid is far more efficient (Daniels, 1973). The dissociation of the hydrochlorous acid is an equilibrium reaction, meaning that the reaction can occur in either direction. Furthermore, the pH of the water affects the direction in which the reaction proceeds, thus influencing the effectiveness of the disinfectant. An increase in pH would mean that there are more H+ ions which would cause the reaction to proceed to the right, meaning that less hypochlorous acid is present in the water. Moreover, a decrease in pH will cause the reaction to proceed to the left, meaning that more hypochlorous acid is produced which increases the effectiveness of the chlorine as a disinfectant. To be able to determine the pH of a solution, the use of acid/ base indicators are needed.

The role of acid/base indicators

In order to keep the pH of pool water in the correct range it is necessary to use an acid/base indicator to test the pH. An acid/base indicator is a substance that gives an accurate indication of the acidity or alkalinity of a solution (Dice, 2008). Also, an indicator is a weak acid represented by HIn (Zumdahl, 2007) and it can be written as an equilibrium expression:

HIn (colourless) â†” H+ + In- (pink)

where the In- is the basic form of the indicator. The HIn and the In- both show a different colour which corresponds to the pH of the solution. As an example, the indicator phenolphthalein is colourless in an acidic solution and pink in a basic solution. This means that the HIn represents the colourless molecules, whereas the In- represents the pinkmolecules. Since an indicator is in equilibrium, an acidic solution would cause an increase in H+ concentration, hence shifting equilibrium to the left. Likewise, in a basic solution the OH- ions cause a decrease in H+, which shifts equilibrium to the right. The equation for an indicator can be written as an equilibrium constant expression.

Ka = [H+] [In-] / [HIn]

This expression can be rearranged to form an equation which is very useful in finding the end point of an indicator, which is the point at which colour change occurs.

Ka / [H+] = [In-] / [HIn]

The ratio between the In- and the HIn will show the colour of the indicator; for example if there is one In- pink molecules for every one hundred colourless it means that the solution will appear colourless. However, for the human eye to detect the colour change, the colour change occurs at a pH where the ratio of In- to HIn is 1: 10 for an acidic solution, whereas for a basic solution the change will occur at a ratio of 10: 1 (Zumdahl, 2007).

There are a variety of indicators all of which are useful for specific pH ranges, and so it is important to use an appropriate indicator for measuring pool water pH. The following table (figure 2) displays four different acid/base indicators that could be possibly used to assist with pool management.

Four Possible Indicators for Testing pH of a pool (figure 2)

Indicator

pH range

Colour shown for Acidic Solution

Colour shown for Basic Solution

Ka

pKa (-log10Ka)

Bromthymol Blue

6. 0-7. 6

Yellow

Blue

1. 0 x 10-7

7. 0

Cresol Red (alkaline)

7. 2-8. 8

Yellow

Reddish-purple

1. 0 x 10-8. 32

8. 32

Phenol Red

6. 8-8. 4

Yellow

Red

1. 0 x 10-7. 9

7. 9

Phenolphthalein

8. 3-10

Colourless

Pink

1. 0 x 10-9. 3

9. 3

From the table it can be seen that phenol red, cresol red and bromthymol blue would all be useful indicators as their pH range is quite close to the pH range of a pool which is 7. 2-7. 8. Since phenolphthalein’s range is 8.-10, this indicator would be the least effective as is not very close to the pool range, whereas the other indicators each have similar ranges that are within the range. To verify the pH at which an indicator changes colour, the equation from above can be used:

Ka = [H+] [In-] / [HIn]

Sample calculation for the indicator phenol red:

x 10-7. 9 = [H+] [In-] / [HIn]

First, the pH at which the indicator will change for an acidic solution will be found. For an acidic solution the colour change will be visible when [In-] / [HIn] = 1/10 :

x 10-7. 9 = [H+] (1) / (10)

[H+] = (1. 0 x 10-7. 9) x 10

= 1. 26 x 10-7

pH = -log(1. 26 x 107â€‘)

= 6. 9

pH = 6. 9, which is close to the actual value of 6. 8. This means that at this point, the colour change will be yellow.

The pH at which the colour change occurs in a basic solution can also be calculated, however, the ratio of In- to HIn will be 10: 1 as there must be more In- molecules for a colour change to occur.

x $10^{-7.9}$ = $[H^+]$ (10) / (1)

$[H^+]$ = (1. 0 x $10^{-7.9}$)/ 10

= 1. 26 x 10^{-9}

pH = -log(1. 26 x 10^{-9})

= 8. 90

pH = 8. 9, which is the point at which the colour change will be red. However, the value is not exactly the same as the actual value because it is an approximation and is not exact. Phenol red's pH range is the closest to the pool's range when compared to the other three indicators, which means that it is the most appropriate for testing pool water. Acid/base indicators are not only important for determining the pH of a solution, but are also significant for finding a pool's buffering capacity, as the pH of a solution must be known.

Buffer solutions

To assist in the maintenance of pool pH, it is necessary to use a buffer solution. A buffer solution is any solution which resists fluctuating changes in pH, making it easier to keep pool water in the appropriate pH range (Hann, 1997). The buffering ability of a pool is dependent on the total alkalinity, which is the measure of the quantity of alkaline substances present in the water (Hann, 1997). Calcium carbonate is the main compound which makes up the total alkalinity and when it is dissolved in water it produces carbonate ions which act as a buffer.

CaCO3 (s) â†” Ca2+ + CO32-

The carbonate ions work as a buffer because they neutralise the H+ ions formed when an acid is added. To determine the buffering ability of a solution, the Henderson-Hasselbalch equation can be used. This equation is derived from the equilibrium constant for the dissociation of a weak acid which is given by the equation:

Ka = ([H+] [A-]) / [HA]

where A- is the conjugate base, and HA is a simple acid. By taking the logarithm of both sides and rearranging it will give the following equation:

-log [H+] = -logKa + log ([A-]/[HA])

Since, -log [H+] = pH and -logKa = pKa, the equation can be written as:

pH = pKa + log ([A-]/[HA])

This equation is known as the Henderson-Hasselbalch equation and can be used in regards to pool chemistry to be able to calculate the buffering capacity, which is the quantity of hydroxide ions (OH-) that can be absorbed by the solution before a significant pH change occurs. Additionally, the magnitude of [HA] and [A-] determine the buffering capacity of a solution. The most effective buffer is one that has a ratio of one, as this will cause no change in pH (Zumdahl, 2007). The following calculation will show a possible application of buffer chemistry for the pool.

pH = pKa + log ([A-]/[HA])

A concentration of 0. 002M Hydrochloric acid is added to a solution with a pH of 7. 6 and a calcium carbonate concentration of 2. 11 x 10-8M. Hypochlorous acid is also present in the water and its pKa is 3. 5 x 10-8.

7. 6 = 3. 5 x 10-8 + log ([2. 11 x 10-8]/[0. 002])

= 7. 46

Therefore, the pH of the solution has decreased, which means that the solution does not have the best buffering capacity. The best buffer solution would need to have a ratio of 1: 1 which would cause the pH to stay about the same.

Conclusion

The chemistry involved in the management of backyard swimming pools is an important aspect and needs to be understood in order to maintain a safe swimming pool environment. A pH range between 7. 2 and 7. 8 is recommended and so an understanding of how to lower and raise the pH is essential. Chlorine can be used as a disinfectant of pool water; however, it needs to be known that the reaction forms hydrochloric acid which lowers the pH. Thus, an addition of a pH increaser such as sodium carbonate is needed as this increases the number of OH- molecules in the water, which increases the pH. Furthermore, the use of pH indicators is necessary in controlling the pH, as they give an accurate reading of the pool's pH. However, each indicator has a different pH range and so it is important to choose the appropriate indicator for the pool. Also, a pools buffering ability is significant in keeping the pool's pH in balance. Poor buffering capacity means that an addition of an acid or a base will cause the pH to dramatically fluctuate, making it difficult to manage a pool. Total alkalinity is the measure of a pool's buffering ability and calcium carbonate is often used to increase the buffering ability.