ChemMatters April 1983 Page 4

CHEMISTRY AT WORK

Swimming Pool Chemistry

by Kathleen J. Dombrink and David O. Tanis

Those who own or maintain swimming pools know that frequent checks should be made on the water quality. One kind of pool "housekeeping" involves the removal of suspended particles such as leaves, dirt, and hair using skimmers and filters. A second kind deals with the much less visible buildup in the water of dissolved pollutants. Dissolved pollutants such as body wastes, algae, and disease-causing bacteria require chemical treatment.

Removing Bacteria

The chemical treatment of swimming pools involves the active disinfectant hypochlorous acid, HOCl. HOCl, a substance also used in drinking water purification and the final step of wastewater treatment, can be produced by the reaction of chlorine gas, Cl_2, with water:

$$Cl_2\ (g) + H_2O\ (l) \Rightarrow HOCl\ (aq) + H^+\ (aq) + Cl^-\ (aq)$$

Because of the corrosive and toxic properties of chlorine gas, sophisticated equipment is needed to handle it. This makes it impractical for home swimming pool use. Therefore, chlorine-containing compounds that serve as a source of HOCl are used instead. Sodium hypochlorite, NaOCl, the active ingredient in household bleach, is a commonly used disinfectant because it reacts with water to produce HOCl:

$$NaOCl\ (aq) + H_2O \Rightarrow HOCl\ (aq) + Na^+\ (aq) + OH^-\ (aq)$$

Other examples of pool sanitizers are calcium hypochlorite, $Ca(OCl)_2$, which is marketed as HTH® and chlorinated isocyanurates, such as trichloroisocyanuric acid.

$Ca(OCl)_2 + 2\ H_2O \Rightarrow 2\ HOCl + Ca(OH)_2$

HOCl is a small molecule that is deadly to bacteria. Because of its size and lack of charge, it can easily penetrate the cell wall of a bacterium. Once it is inside, both the chlorine and the oxygen from the hypochlorous acid molecule oxidize or "burn out" the interior of the bacterium by breaking down the bacterium's protein.

Maintaining Chemical Balance

The amount of HOCl available in a swimming pool depends on several factors. Immediately after treatment, there is plenty of HOCl in a pool. The level of HOCl decreases as it is used in destroying bacteria, algae, and other organic substances in the pool. Also, the amount of HOCl present in the water depends on the pH of the water in the pool.

To see how changes in pH affect the amount of HOCl available, we must understand that HOCl dissociates (breaks apart) to form hydrogen ion, H^+, and hypochlorite ion, OCl^-, in water:

$HOCl\ (aq) \Rightarrow H^+\ (aq) + OCl^-\ (aq)$ (1)

H^+ and OCl^- can also recombine to produce HOCl molecules:

$H^+\ (aq) + OCl^-\ (aq) \Rightarrow HOCl\ (aq)$ (2)

Because reaction 2 is just the reverse of reaction 1, and because both reactions are occurring at the same time, chemists usually write one equation to represent both processes.

$HOCl\ (aq) \quad \Leftrightarrow \quad H^+\ (aq) \quad + \quad OCl^-$

(Hypochlorous acid) (Hydrogen ion) (Hypochlorite ion)

When these two reactions occur at the same rate, we say that an equilibrium exists.

When the pH of the water in the pool is lowered, that is when more H^+ is added to the system, the extra H^+ reacts with some of the OCl- already present to produce more HOCl. The concentration of HOCl available in the pool is increased and we say "the equilibrium is shifted to the left." If the pH is raised by adding a base, the extra hydroxide ion, OH^-, combines with some of the H^+ in the pool to produce water:

$H^+\ (aq) + OH^-\ (aq) \Rightarrow H_2O\ (l)$

Some of the available HOCl in the pool then breaks apart to form more H^+ (to compensate for the H^+ that was used up by the OH^-) and more OCl^-. We say that the "equilibrium is shifted to the right."

Figure 1 shows how shifts in pH change the concentrations of OCl^- and HOCl.

The Ideal pH Level

The ideal equilibrium distribution is equal concentrations of HOCl and OCl^-. The table shows that a pH of 7.5 maintains this balance. If the pH is held in the range from 7.2 to 7.8, a suitable distribution of HOCl and OCl^- is provided. If the pH is lower than 7.2, the high concentration of HOCl is very irritating to the eyes of swimmers. Also, the growth of algae flourishes in this acid range. If the pH is higher than 7.8, too much of the disinfectant is present as OCl^-, which is decomposed rapidly by sunlight.

The pH is adjusted by adding acid or base to the pool water. If the pH is too high (if the pool water is too basic), hydrochloric (muriatic) acid, HCl, or sodium bisulfate, $NaHSO_4$, can be added to the water to react with this excess base. If the pH is too low (if the pool is too acidic), sodium carbonate, Na_2CO_3, added to the pool will react with the excess acid and bring the pH back up to an acceptable value.

Pool care involves both physical and chemical treatments. Although the tests used to determine the necessity of chemical treatment do not require an understanding of the chemistry involved, some knowledge of acid-base chemistry, pH, and equilibrium concepts provides the pool owner with the logic behind these chemical treatments. This knowledge also helps to ensure the safety of all who use the pool.

SIDE BARS

Using the relative sizes of the symbols to show concentration, we can show the equilibrium at a pH of 7.5 as:

$HOCl \Leftrightarrow H^+ + OCl^-$

If the pH drops below 7.5, the equilibrium shifts to the left because of the increase in H^+ concentration:

$HOCl \Leftrightarrow H^+ + OCl^-$

If the pH rises, the equilibrium shifts to the right to try to replace the H^+ consumed by base:

$$HOCl \Leftrightarrow H^+ + OCl^-$$

CAPTION

Effects of pH changes

REFERENCES

Linda, F. W.; Hollenbach, R.C. "The Backyard Pool." *Sciquest*, 52(5):7-9, May/June 1979.

Faust, J. P.; Gower, A.H. "Treatment of Swimming Pools." *Kirk-Othmer Encyclopedia of Chemical Technology*, Vol. 22, 2nd ed. N.Y.: Wiley and Sons, 1970.

Faust, J. P.; Waldvogel, R.L. *The HTH® Water Book*. Stamford, Connecticut: Olin Chemicals, 1976.