The Chemistry of Swimming Pool Maintenance   ɯ

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The chemistry involved in swimming pool maintenance provides many potential applications in undergraduate chemical education. For example, students can learn the importance of pH in water chemistry because pH affects chlorine sanitation and calcium balance. Both chlorination and calcium solubility provide practical examples of chemical equilibrium at work. The reactions of ammonia with chlorine introduce unusual redox chemistry. There are many obvious applications of pool chemistry in an analytical chemistry course, and the effect of temperature on pool equilibria is a possible physical chemistry topic. The purpose of this paper is to explain the basic chemistry behind the common practices involved in swimming pool maintenance. We hope it stimulates the inclusion of pool chemistry throughout the curriculum.

As a topic for discussion in general chemistry classes, swimming pool chemistry is both interesting and approachable. Swimming pools are enjoyed by almost everyone—swimmers and nonswimmers alike—and most people are aware that chlorine is usually added to pool water to keep swimming pools clean because they have experienced the effects of chlorination on their eyes and nose. Pool owners know that, in addition to chlorine, they must measure and control a number of other factors that affect the quality of their pool water: pH, water hardness, total alkalinity, and total dissolved solids. Pool distributors market a wide array of compounds and test materials to help pool owners. According to data from the Association of Pool and Spa Professionals, there are roughly 8 million residential pools in the United States, and each year pool owners spend about 4 billion dollars on their maintenance (1).
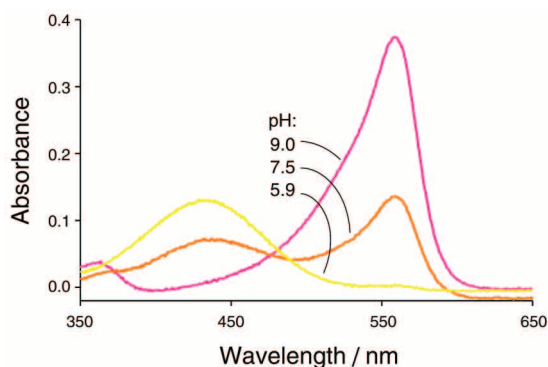
Despite the fact that pool chemistry is an interesting application of chemical principles, there has been only one paper in this *Journal* about pool maintenance, and its discussion is outdated (2). There are reports of laboratory experiments designed around certain aspects of pool chemistry (3a–3d), and one recent discussion of chlorination (4), yet none which focus on pool maintenance.

At the center of pool chemistry is pH, which affects the balance of two important processes: the equilibrium between hypochlorous acid and hypochlorite ion, and the equilibrium between calcium ions in solution and calcium carbonate in the cement or plaster liner of many pools. Hypochlorous acid is the most effective antibacterial species formed by chlorine, and so, other things being equal, the pH of pool water should be low enough to ensure that a good portion of the dissolved hypochlorite is protonated.
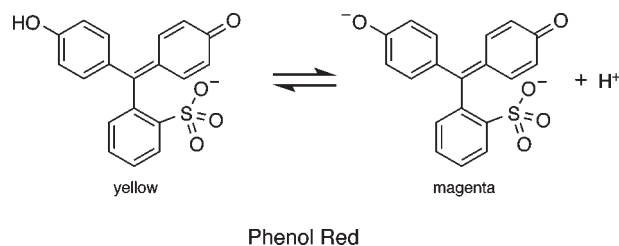
$$\text{HOCl (aq)} \;\rightleftharpoons\; \text{OCl}^- \text{(aq)} + \text{H}^+ \text{(aq)}$$
$$\text{hypochlorous} \qquad \text{hypochlorite}$$
$$\text{acid}$$
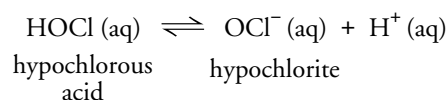
Conversely, too much acid can dissolve calcium carbonate, and you certainly don't want your swimming pool to dissolve!

$$2\text{H}^+\text{(aq)} + \text{CaCO}_3 \;\rightleftharpoons\; \text{H}_2\text{O} + \text{CO}_2 + \text{Ca}^{+2}\text{(aq)}$$
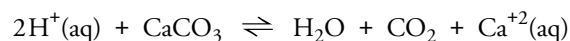
To balance these processes, it's critical to hold the pH of the pool water within strict limits.

Measuring Pool pH without a pH Meter

Phenol red is the indicator of choice. Pool test kits usually provide phenol red in solution or impregnated into test strips, and provide a series of color references to read the pH. At pH 7.5 a solution of phenol red will appear orange due to the mixture of yellow (acid) and magenta (base) forms of the indicator.


Phenol Red

Figure 1. The absorption spectra of phenol red at various pH values. Spectra were obtained using an Ocean Optics USB2000 UV–vis spectrometer with 25 µm slits. The solutions were buffered and contained the same concentration of phenol red. Notice that the absorptivity of the base form at its wavelength maximum is about three times that of the acid form.

Although the pK_{a_2} of phenol red is 7.96 (5), most of the color change takes place around pH 7.5. The visible absorption spectra of phenol red at different pH values (Figure 1) show that the absorptivity of the conjugate base is about three times greater than that of the acid form, which is the reason why the color change is most pronounced at pH 7.5.

Adjusting Pool pH

To decrease pool pH either hydrochloric acid or sodium hydrogen sulfate ("dry acid") can be added to the pool water. To increase the pH, sodium carbonate should be used; sodium bicarbonate will increase total alkalinity but will not move the pH efficiently.

## The Effect of pH on Chlorine Disinfection

The pK_a of hypochlorous acid is 7.53 (6). Although both HOCl and OCl⁻ can kill bacteria, hypochlorous acid is more potent (7); as a neutral species it will cross the cell membrane faster. Once inside the cell, hypochlorous acid inactivates key enzymes by oxidizing side chains, especially those containing sulfur (8).
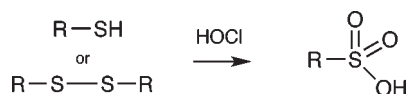
Above pH 7.5 most of the hypochlorous acid is ionized to form hypochlorite ion, so the effectiveness of the chlorine protection is reduced. On the other hand, hypochlorous acid is more easily lost from pool water by outgassing and sunlight degradation, so it is not good to have all of the active chlorine as the acid. For this and other reasons the pH of pool water is kept close to the pK_a of hypochlorous acid.

Sources of Chlorine for Pools

There are a variety of chemicals that can be added to pool water to generate the desired hypochlorous acid. Pool distributors will usually tell you that there are three kinds of chlorine: solid, liquid, and gas. Of course, chlorine, Cl_2, is a gas at room temperature and pressure, not a liquid or a solid. Gaseous chlorine is sometimes used for large-scale chlorination, such as at a municipal pool. Private pool owners usually use either "liquid chlorine", NaOCl in aqueous solution, or "solid chlorine", which can either be cakes or tablets of $Ca(OCl)_2$ or chloroisocyanurates marketed under the tradenames Dichlor and Trichlor. Calcium hypochlorite
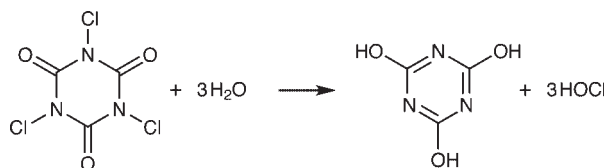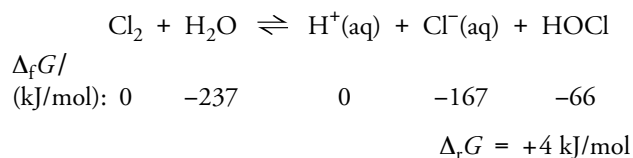

also adds calcium to pool water, which can be an advantage when the water available to fill the pool is soft. Dichlor and Trichlor are called "stabilized chlorine"; they react with water to form cyanuric acid and hypochlorous acid. Their advantage is that cyanuric acid protects the hypochlorous acid from sunlight degradation as discussed below.

Aqueous Chlorine Chemistry

Chlorine gas at 1 atmosphere and 25 °C will form a saturated aqueous solution of 0.73% (wt/wt) or 0.092 M Cl_2. In a saturated solution roughly one-third of the dissolved chlorine reacts with water to form hypochlorous acid, leading to final concentrations of $[Cl_2] = 0.062$ M and $[HOCl] = [Cl^-] = 0.030$ M (9); the equilibrium actually favors chlorine and water, as can be seen from the Gibbs free energies (10) of the species

$$Cl_2 + H_2O \rightleftharpoons H^+(aq) + Cl^-(aq) + HOCl$$

$\Delta_f G/$
(kJ/mol): 0   −237   0   −167   −66

$$\Delta_r G = +4 \text{ kJ/mol}$$

$$\frac{[H^+][Cl^-][HOCl]}{[Cl_2]} = 4 \times 10^{-4}$$

or the equilibrium expression. Of course, pool water is not saturated with chlorine. For dilute solutions of chlorine above pH 4, the equilibrium is displaced strongly to the right, and very little free chlorine exists in solution (7). The reaction of chlorine with water is both a hydrolysis reaction and a disproportionation reaction. Because the reaction releases hydrochloric acid, the addition of chlorine to pool water will lower the pH.

The solubility of chlorine can be vastly increased by dissolving the chlorine in strong NaOH solution; most household bleaches are solutions of 5% NaOCl.
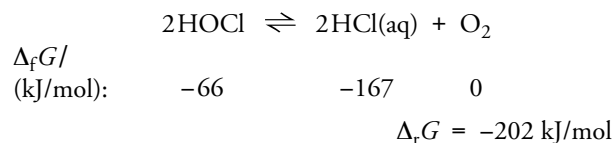
$$Cl_2 + 2NaOH(aq) \rightleftharpoons NaCl(aq) + NaOCl(aq) + H_2O$$
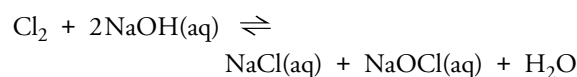
The addition of hypochlorite to pool water increases the pH by releasing hydroxide ions.

$$OCl^-(aq) + H_2O \rightleftharpoons HOCl + OH^-(aq)$$
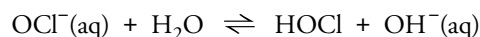
In addition, if bleach is the source of the hypochlorite, its excess sodium hydroxide will also raise the pH.

Outdoor pools can lose chlorine protection during the daytime: it is estimated that direct summertime sunlight can destroy 90% of free chlorine in two hours (11). Sunlight destroys HOCl, presumably by a sequence of reactions that ultimately leads to oxygen gas (11, 12), a reaction that is exoergic at standard conditions.

$$2HOCl \rightleftharpoons 2HCl(aq) + O_2$$

$\Delta_f G/$
(kJ/mol):   −66   −167   0

$$\Delta_r G = -202 \text{ kJ/mol}$$

The reactions are probably initiated by the photolysis reaction $HOCl + h\upsilon \rightarrow HO\cdot + Cl\cdot$.

Cyanuric acid stabilizes chlorine by preventing sunlight decomposition of HOCl, as it appears to sequester chlorine in a form that is impervious to photolysis. Cyanuric acid can be added directly to pool water, or it can be added with chlorine using Dichlor or Trichlor. The recommended concentration of cyanuric acid in pool water is 30–50 ppm. Pinto and Rohrig have discussed the chemistry of chloroisocyanurates

in this *Journal (4),* and developed study questions for the topic. Clyde has discussed the chemistry of cyanuric acid and its derivatives in this *Journal (3c).* Donnelly has described several general chemistry experiments designed to investigate the protection of hypochlorous acid by cyanuric acid *(3d).*

Free Chlorine and Combined Chlorine

That "chlorine pool" smell is really NH_2Cl, monochloramine, which is produced by the reaction of hypochlorous acid and ammonia.

$$HOCl + NH_3 \rightleftharpoons NH_2Cl + H_2O$$
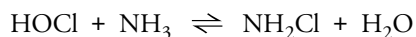
(Dangerous amounts of chloramines can be produced by mixing household bleach with ammonia-based cleaners. Many bleaches and cleaning solutions bear warnings against this practice.) In pool water the most likely sources of ammonia are urine and sweat. Monochloramine is a weaker disinfectant than HOCl. At low concentrations it can be a useful disinfectant in municipal water supplies because it is long-lasting *(7),* but its irritating smell makes it undesirable in pool water.

The sum of chlorine present as Cl_2, HOCl, and OCl^- is called free chlorine. Chlorine present as the chloramines NH_2Cl and $NHCl_2$ is called combined chlorine. The sum of free chlorine and combined chlorine is total chlorine. For effective sanitation, total chlorine should be maintained between 1–3 ppm with the bulk of this as free chlorine. Combined chlorine concentrations in excess of 0.2 ppm impart a discernable "chlorine" odor to the pool water and cause a burning sensation of the eyes. This condition is routinely tolerated in heavily-used public facilities, yet it can be avoided altogether simply by keeping combined chlorine values under control.

Pool Shocking

When the combined chlorine rises above an acceptable value, it is time to "shock" your pool. Shocking, also called superchlorination or "breakpoint chlorination" *(7, 13),* requires a dramatic increase in chlorine, up to 10 ppm, which causes further oxidation of monochloramine, leading to $NHCl_2$ and then NCl_3 which decomposes to N_2. The overall process of breakpoint chlorination converts ammonia to gaseous nitrogen:

$$2NH_3 + 3Cl_2 \rightleftharpoons N_2 + 6HCl$$
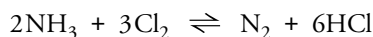
Other oxidizers such as potassium peroxymonosulfate can be used for pool shocking. Many pool instructions describe shocking as "burning the ammonia" out of the water, and in the sense that it is an oxidation of nitrogen in ammonia, the metaphor is not misplaced.

Measuring Chlorine

Test kits for pool chlorine should be able to measure both free and total chlorine residual. *N,N*–diethylphenylenediamine, DPD, which forms a colored product due to oxidation, can be used for both measurements. DPD is oxidized directly by free chlorine to form a colored radical species called a Würster dye (*14*, p 1174):
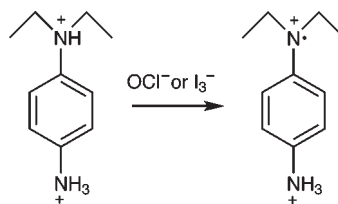
Chloramines do not oxidize DPD. To measure total chlorine, I^- is added to the test solution. I^- is oxidized to I_3^- by chloramines, then I_3^- oxidizes DPD just as free chlorine does. Note that there is no direct measure of combined chlorine.

Maintaining Good Balance

Soft water or acidic water could leach minerals from metal pipes or calcium-based pool liners. Such water is called "aggressive" or "corrosive". Water high in calcium could precipitate calcium carbonate, leading to cloudy pool water or clogged filters. Such water is called "scaling". Water hardness and alkalinity must be adjusted so that a close balance is maintained between aggressive water and scale-forming water.

Measuring Calcium Hardness

Water hardness is primarily a measure of the calcium and magnesium ion concentration in a water sample; since calcium is usually the predominant ion, hardness is expressed as a concentration of $CaCO_3$. Calcium hardness (CH) is typically measured by titrating a fixed volume of pool water with EDTA at a moderately basic pH using a metallochromic indicator, such as Murexide. A poolside procedure that doesn't require special-purpose apparatus is conveniently built around a drop-count titration. A multiplier for converting the number of drops to ppm $CaCO_3$ is readily determined by titrating a $CaCO_3$ standard. The CH of pool water should be between 100–500 ppm $CaCO_3$. CH can be increased by adding $CaCl_2$ to the pool water; decreasing CH requires partial draining and refilling with water of lower Ca concentration.

Measuring Total Alkalinity

Total alkalinity (TA) is a measure of the buffer capacity of a water sample. The primary buffering component present in swimming pool water is carbonate, so TA is primarily a measure of dissolved carbonate. Note, however, that at neutral pH the predominant carbonate-containing species will be the HCO_3^- ion. Like CH, TA is expressed as a concentration of $CaCO_3$. TA can be measured by a drop-count titration in which a fixed volume of pool water is titrated with standard acid (usually dilute H_2SO_4) to the bromocresol green endpoint. An appropriate multiplier for converting the drop count to ppm $CaCO_3$ can be obtained by titrating a $CaCO_3$ or $NaHCO_3$ standard. (The CH in ppm $CaCO_3$ need not match or bear any discernable relationship to TA in ppm $CaCO_3$; the two titrations are independent. In pool water calcium is usually present in higher molar concentration than carbonate because chloride is the predominate counter ion.) Pool water should have a TA between 80–120 ppm $CaCO_3$. Increase TA by adding sodium bicarbonate; decrease it by adding acid.

Measuring Total Dissolved Solids

Total dissolved solids (TDS) is a measure of the ionic strength of a water sample. While all the ions present in the pool water contribute to its TDS, primary contributors are usually Na^+ and Cl^-, so TDS is ordinarily expressed as ppm of NaCl. Compared to CH and TA, TDS exerts a very weak effect on calcium carbonate solubility; however, it can vary widely during the swimming season. For example, at the beginning of summer an outdoor pool filled with fresh well water might exhibit a TDS value of a few hundred ppm NaCl. If sodium hypochlorite is used for disinfection, then over the course of several months the TDS could rise to 2000 ppm NaCl. The only way to lower TDS would be to drain the water from the pool and start over with fresh well water. In general it is necessary to make do with the TDS value one has.

TDS is obtained by measuring the electrical conductivity of a water sample. The most convenient poolside method for making this measurement is a commercially available, battery-powered conductivity meter calibrated in ppm NaCl.

Using Test Strips

Many pool supply stores carry test strips that can simultaneously measure pH, free and total chlorine, TA, and CH. Test strips are excellent for diagnosing pool problems, but are probably not sufficiently accurate to prepare a chemical prescription for correcting pool chemistry. Tests strips could be used to develop interesting laboratory experiments on simulated pool water. The analytical chemistry and manufacturing technology behind these test strips deserve a separate paper.

The Langelier Saturation Index

To achieve balanced calcium carbonate solubility in your pool water, you need the right mix of H^+, HCO_3^-, and Ca^{2+}. The balance is judged using the Langelier saturation index (LI), which is the difference between the actual pH and the pH where $CaCO_3$ would neither dissolve nor precipitate.

$$LI = pH - pH_s$$

The pH of balanced solubility, pH_s, is computed using a method published by Langelier in 1936 for estimating the corrosive or scale-forming potential of water in steam pipes (14, p 1194; 15, 16). The pH_s is a strong function of TA and CH, while temperature and TDS affect pH_s to a lesser extent.

If the pool water's LI is positive, the water is "scaling" and tends to precipitate calcium carbonate; if the LI is negative, the water is "aggressive" and tends to dissolve calcium carbonate. Pool water should be balanced or slightly scale forming.

Deriving the Langelier Saturation Index Equation

The following derivation explains the equation and tables for the calculation of pH_s that appear in ref 14, p 1194.

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{-2}$$
$$pK_{a_2} = 10.33$$

$$CaCO_3 \rightleftharpoons Ca^{+2} + CO_3^{-2}$$
$$pK_{sp} = 8.35$$
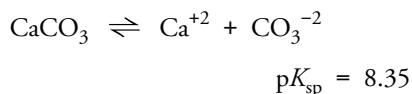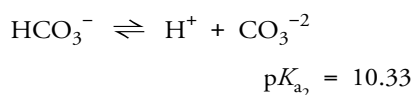
Table 1. Measurements and Values for Calculating the Langelier Saturation Index of Pool Water

Parameter Measured	Measurement Values	Contribution to pH_s of Balanced Solubility[a]
Temperature	25°C	2.00
Total Dissolved Solids	200 ppm	9.83
Calcium Hardness	50 ppm	1.70
Total Alkalinity	60 ppm	1.76

[a]See ref 14.

Solve the first equilibrium for $[H^+]$ (since we seek pH_s). Solve the second equilibrium for $[CO_3^{2-}]$ and substitute in the first equation.

$$\left[H^+\right]_s = \frac{K_{a_2}}{K_{sp}}\left[HCO_3^-\right]\left[Ca^{+2}\right]$$

CH and TA are expressed in ppm $CaCO_3$; the molar mass of $CaCO_3$ is 100 g mol^{-1}. Substituting $[Ca^{2+}] = 1 \times 10^{-5}$ CH and $[HCO_3^-] = 2 \times 10^{-5}$ TA yields

$$\left[H^+\right]_s = \frac{K_{a_2}}{K_{sp}}\left(2 \times 10^{-10}\right) \times TA \times CH$$

$$pH_s = pK_{a_2} - pK_{sp} + 9.70 - \log_{10}TA - \log_{10}CH$$

The effect of temperature is rolled into the combined value of $pK_{a_2} - pK_{sp}$ in Table 1 of ref 14. The effect of ionic strength is rolled into Table 2 of ref 14, which also contains the combined conversion factors for CH and TA to molarity of calcium and bicarbonate (the constant 9.70 in the formula above). Table 3 of ref 14 contains logarithmic values for the concentrations of TA and CH when they are expressed in ppm.

Calculating the Langelier Saturation Index

Let's assume that we have made measurements on pool water and wish to compute its LI. Table 1 shows the assumed measurements and the corresponding values read from the tables in the *Hach Handbook (14)*.

For this sample of pool water, the pH_s = 2.00 + 9.83 − 1.70 − 1.76 = 8.37. If pH of the pool is 7.62, which is about right for proper chlorination, then the LI = −0.75, and the pool water is moderately aggressive.

To confirm that $CaCO_3$ should dissolve in this pool water, we must show that

$$\left[Ca^{+2}\right]\left[CO_3^{-2}\right] < K_{sp} \qquad K_{sp} = 3.3 \times 10^{-9}$$

$$\left[Ca^{+2}\right] = \frac{50\ mg\ CaCO_3/L}{100\ mg/mmol}$$

$$= 0.5\ \frac{mmol}{L} = 5 \times 10^{-4}\ M$$

TA essentially measures $[HCO_3^-]$, which is double the concentration of the "$CaCO_3$" alkalinity. $[HCO_3^-] = 12 \times 10^{-4}$ M.

Table 2. Recommended Chemical Parameters for Pool Water Maintenance

Chemical Parameter	Desired Range, ppm	To Increase Parameter, Add:	To Decrease Parameter, Add:
pH	7.4–7.6[a]	Na_2CO_3	HCl
Free Cl	1–3	OCl^-; Dichlor	—
Calcium Hardness	100–500	$CaCl_2$	H_2O
Total Alkalinity	80–120	$NaHCO_3$	HCl
Total Dissolved Solids	<2000	—	H_2O
Cyanuric Acid	30–50	Cyanuric acid; Dichlor	—

[a]Dimensionless, not presented in ppm.

Using the carbonate/bicarbonate equilibrium and the pH we can solve for the carbonate concentration

$$HCO_3^- \;\rightleftharpoons\; H^+ + CO_3^{-2}$$

$$K_{a_2} = 4.7 \times 10^{-11}$$
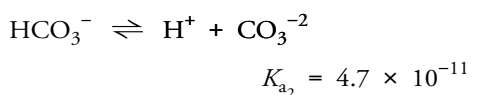
$$\left[CO_3^{-2}\right] = K_{a_2} \frac{\left[HCO_3^-\right]}{\left[H^+\right]} = 2.2 \times 10^{-6}$$

$$\left[Ca^{+2}\right]\left[CO_3^{-2}\right] = \left(5 \times 10^{-4}\right)\left(2.2 \times 10^{-6}\right)$$

$$= 1.2 \times 10^{-9} \quad < \quad K_{sp}$$

Since the ion product is just below K_{sp}, this water is not saturated and will tend to dissolve calcium carbonate. At higher pH there would be a higher carbonate concentration, and the water would be less corrosive. If the pH of the pool is already correct, then the appropriate action is to increase the calcium concentration by adding $CaCl_2$. Bieron et al. have designed experiments that lead students to compute the LI of pool water *(3a)*.

Conclusion: The Pool Doctor Says …

There are certainly aspects of pool maintenance that have not been covered in this paper. Calcium carbonate solubility is not a serious issue for private pools constructed with vinyl liners; however, vinyl liners have their own set of maintenance concerns such as puncturing, splitting, staining, and loss of plasticizer. There are alternatives to chlorine disinfection— bromine can be used, and often is used in hot water spas because it is less likely to outgas. There are also some expensive disinfection procedures based on silver and copper ions. Algae can be a problem, and pool product suppliers sell a variety of algaecides that maintain the attractiveness of pool water. But for most large swimming pools, maintaining chlorine and calcium carbonate balance are the key concerns. We hope this

paper has provided a chemically informed view of the challenge of pool maintenance. To that end, we offer Table 2 as a summary of maintenance procedures.

ᵂSupplemental Material

An annotated bibliography of swimming pool chemistry resources is available in this issue of *JCE Online*.

Literature Cited

1. Economic Impact of the Pool and Spa Industry. Association of Pool and Spa Professionals: Alexandria, VA, 2005; *http://www.iafh2o.org/IAF_Statistics.asp* (accessed May 2007).
2. DeWindt, E. A. *J. Chem. Educ.* **1936**, *13*, 576.
3. (a) Bieron, Joseph F.; McCarthy, Paul J.; Kermis, Thomas W. *J. Chem. Educ.* **1996**, *73*, 1021–1022. (b) Hardee, J. R.; Long, J.; Otts, J. *J. Chem. Educ.* **2002**, *79*, 633–634. (c) Clyde, D. D. *J. Chem. Educ.* **1988**, *65*, 911. (d) Donnelly, S. J. Swimming Pool Chemistry Lab. *http://www.azwestern.edu/Office_of_the_President/Institutional_Research/swimming_pool_chemistry.html* (accessed May 2007).
4. Pinto, G.; Rohrig, B. *J. Chem. Educ.* **2003**, *80*, 41–44.
5. Freiser, H.; Fernando, Q. *Ionic Equilibria in Analytical Chemistry;* John Wiley and Sons: New York, 1963; p 325.
6. Harris, D. C. *Quantitative Chemical Analysis;* W. H. Freeman and Co: New York, 2002.
7. Sawyer, C. N.; McCarty, P. L.; Parkin, G. F. *Chemistry for Environmental Engineering and Science,* 5th ed.; McGraw-Hill: New York, 2003; Chapter 20, pp 571–586.
8. Talaro, K. P.; Talaro, A. *Foundations in Microbiology,* 4th ed.; McGraw-Hill: New York, 2002; p 336.
9. *The Merck Index,* 13th ed.; Merck & Co, Inc.: Rahway, NJ, 2001; p 361.
10. Standard thermochemical values for gas phase HOCl from *CRC Handbook of Chemistry and Physics,* 73rd ed.; CRC Press: Boca Raton, FL, 1992; p 5-12.
11. Lowry, R. W. *Pool Chlorination Facts;* RJ Communications: New York, 2003; Chapter 18, pp 151–156.
12. O'Leary, D. Chlorine. *http://www.ucc.ie/academic/chem/dolchem/html/elem/elem017.html* (accessed May 2007).
13. Chemistry of Breakpoint Chlorination, Margerum Research Lab Web Page. *http://www.chem.purdue.edu/margerum/breakcl2.html* (accessed May 2007).
14. *Water Analysis Handbook,* 4th ed., 2nd rev.; Hach Company: Loveland, CO, 2003. *http://www.hach.com/fmmimghach?/CODE%3AEX_LANGAGG1428%7C1* (accessed May 2007).
15. Langelier, W. F. *Journal of the American Water Works Association* **1936**, *28*, 1500.
16. Langelier Saturation Index Web Site. *http://www.corrosion-doctors.org/Cooling-Water-Towers/Index-Langelier.htm* (accessed May 2007).