

Swimming Pool Water Balance

Part 8: The Thermodynamic Basis of the Saturation Index

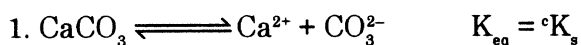
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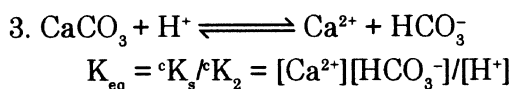
Thermodynamics (i.e., the laws governing the conversion of heat to and from other forms of energy) is the logical discipline for the mathematical treatment of chemical reactions in homogeneous and heterogeneous systems. The sign of the free energy change as an indicator of the direction of a reaction was known in 1886 (Van't Hoff) under the name "reaction isotherm". The free energy change is a measure of the useful energy available from a system. When applied to solutions of calcium carbonate, the expression for the free energy change for a reaction readily and naturally leads to the calcium carbonate saturation index. The equation that bears Langelier's name, derived from ionic equilibria, is not novel. Therefore, a more appropriate name would be calcium carbonate saturation index as Langelier originally named it (Langelier 1936).

Theory

The aqueous solubility equilibrium of calcium carbonate can be expressed by the following reactions:



Overall:



where: ${}^{\circ}K_s$ is the concentration solubility product constant of calcium carbonate and ${}^{\circ}K_2$ is the second concentration ionization constant of carbonic acid.

The Gibbs free energy change (ΔG) for the above reaction is given by (Stumm and Morgan 1996):

$$4. \Delta G = 2.3RT \text{ Log } (Q/K)$$

where: ΔG is the free energy (Joules per mol) of dissolution of calcium carbonate, R is the gas constant ($8.314 \text{ J deg}^{-1} \text{ mol}^{-1}$), T is the absolute temperature in kelvins (i.e., $273 + {}^{\circ}\text{C}$), Q represents the actual composition, and K the equilibrium composition. The ratio Q/K represents the departure of the system from equilibrium. Rearrangement leads immediately to the calcium carbonate saturation index (SI):

$$5. \Delta G / (2.3RT) = \text{Log } (Q/K) = \text{SI}$$

That this is so can be shown by substitution of the appropriate chemical terms from equation 3, where the subscripts a and e denote actual and equilibrium concentrations, i.e., $Q = [\text{Ca}^{2+}]_a [\text{HCO}_3^-]_a / [\text{H}^+]_a$ and $K = [\text{Ca}^{2+}]_e [\text{HCO}_3^-]_e / [\text{H}^+]_e$.

$$6. \text{SI} = \text{Log} [\text{Ca}^{2+}]_a [\text{HCO}_3^-]_a [\text{H}^+]_e / [\text{Ca}^{2+}]_e [\text{HCO}_3^-]_e [\text{H}^+]_a$$

Since $[\text{Ca}^{2+}]_e [\text{HCO}_3^-]_e / [\text{H}^+]_e = {}^{\circ}K_s / K_2$ equation 6 simplifies to:

$$7. \text{SI} = \text{Log} [\text{Ca}^{2+}]_a [\text{HCO}_3^-]_a {}^{\circ}K_s / ([\text{H}^+]_a {}^{\circ}K_s)$$

Setting $[\text{HCO}_3^-]_a \cong [\text{Alk}]_a$ and expanding the right side of equation 7, gives the calcium carbonate

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saturation index with concentrations in mol/L:

$$8. SI = pH_a + \text{Log} [Ca^{2+}]_a + \text{Log} [Alk]_a + \text{Log } {}^cK_2/K_s$$

Introduction of factors for converting alkalinity from mol/L to ppm $CaCO_3$ (-4.7) and calcium from mol/L to ppm $CaCO_3$ (-5.0), a value of -2.25 for $\text{Log } {}^cK_2/K_s$ at 0°C and an ionic strength correction of -0.34 for 1000 ppm TDS and a correction factor for the temperature dependence of K_2/K_s (TC) gives the familiar and updated form of the calcium carbonate saturation index (see part 7 of this series).

$$9. SI = pH + \text{Log} [Hard] + \text{Log} [Alk] + TC - 12.29$$

Another familiar form of the calcium carbonate saturation index is obtained by setting $[Ca^{2+}]_a = [Ca^{2+}]_e$, $[HCO_3^-]_a = [HCO_3^-]_e$, and $pH = \text{Log } 1/[H^+]$ in equation 6:

$$10. SI = \text{Log} ([H^+]_e/[H^+]_a) = pH_a - pH_e = pH_a - pH_s$$

where pH_e is equivalent to pH_s i.e., pH at calcium carbonate saturation.

Equation 10 is the form that Langelier originally expressed the saturation index. He did not transform it to a form such as equation 9 which is often referred to as the Langelier formula or Langelier saturation index. The concept of saturation index for calcium carbonate follows naturally from thermodynamic principles, which were developed in the nineteenth century. Thus, the so-called Langelier Saturation Index, which was derived from ionic equilibria, is not novel. Therefore, a more appropriate name would be calcium carbonate saturation index as Langelier originally called it (Langelier 1936).

The Gibbs free energy change (equation 4) has always been the criterion for judging the spontane-

ity of chemical reactions via the sign of ΔG , as shown by the data in Table 1 (Stumm and Morgan 1996).

References

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- Van't Hoff (1886) from Glasstone, Samuel. *Thermodynamics for Chemists*. (D. Van Nostrand, New York, NY 1947) p. 283.
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About the Author

Now retired, **Mr. Wojtowicz** was a senior consulting scientist for Olin Corp. Seventeen of his 47 years of industrial experience was spent in the swimming pool chemical area and primarily involved swimming pool chemistry and process and product research on calcium hypochlorite, trichloroisocyanuric acid, and sodium dichloroisocyanurate. He holds over 55 U. S. patents and has published over 40 technical papers. He is currently a chemical consultant (Chemcon) residing at 60 Philson Court, Cheshire, CT 06410, phone #203-272-1479. His areas of expertise include swimming pool chemistry, manufacture and product and process development in hypochlorites and chloroisocyanurates, alternate sanitizers and sanitation systems (ozone, hydrogen peroxide-UV, bromine, etc.), chloramines and bromamines, computer programming, and expert witnessing.

$\Delta G = 2.3RT \text{Log} (Q/K)$	Reaction Possibilities
<0 (negative, $Q < K$)	reaction is possible - $CaCO_3$ can dissolve
0 ($Q = K$)	system is in equilibrium - $CaCO_3$ will not dissolve or precipitate
>0 (positive, $Q > K$)	reaction not possible in forward direction, but possible in reverse direction, i.e., $CaCO_3$ can precipitate

Table 1 - Reaction Possibilities from Gibbs Free Energy Change
 $CaCO_3 + H^+ \rightleftharpoons Ca^{2+} + HCO_3^-$