Example Questions: The Carbonate System

1. A water sample has a measured total alkalinity of 50. ppm $CaCO_3$. Calculate the concentration of all contributing species if the pH of the water sample is;

i) 7.00 ii) 10.00

$[alk]_T = [HCO_3^-] + [OH^-] + 2[CO_3^{2-}]$ ← acid neutralizing capacity in mols H^+/L

$$50.\ \frac{mg\ CaCO_3}{kg} \times \frac{1\ mol}{100.08\ g} \times \frac{1\ kg}{1\ L} \times \frac{2\ mol\ H^+}{1\ mol\ CaCO_3} \times \frac{1\ g}{10^3\ mg} = 1.0 \times 10^{-3}\ \frac{mol}{L}$$

pH 7

$[OH^-] = 10^{-7.0}$ $[CO_3^{2-}]$ from Ka_2 expression, but negligible at pH 7; $[CO_3^{2-}] = \left(\frac{Ka_2}{[H^+]}\right)[HCO_3^-]$

$\therefore\ [HCO_3^-] = 1.0 \times 10^{-3}\ M$, $[OH^-] = 1.0 \times 10^{-7}\ M$, $[CO_3^{2-}] = 4.7 \times 10^{-11}\ M$

pH 10

$[OH^-] = 10^{-4.0}$

$$[alk]_T = [HCO_3^-] + [OH^-] + 2\left(\frac{Ka_2}{[H^+]}\right)[HCO_3^-] = 1.0 \times 10^{-3}\ M$$

$$[HCO_3^-]\left(1 + \frac{2\,Ka_2}{[H^+]}\right) = 1.0 \times 10^{-3} - [OH^-]$$

$[HCO_3^-] = 4.6 \times 10^{-4}\ M$, $[CO_3^{2-}] = 2.2 \times 10^{-4}\ M$, $[OH^-] = 1.0 \times 10^{-4}\ M$

2. Compare the pH and T_{alk} (as ppm $CaCO_3$) of the following two solutions.

i) 1.00×10^{-3} M NaOH ii) 0.100 M $NaHCO_3$

i) **pH = 11.0**

$[alk]_T = 1.0 \times 10^{-3}\ \frac{mol\ H^+}{L}$

$$T_{alk} = 1.0 \times 10^{-3}\ \frac{mol\ H^+}{L} \times \frac{100.08\ g}{1\ mol\ CaCO_3} \times \frac{1\ mol\ CaCO_3}{2\ mol\ H^+} \times \frac{10^3\ mg}{g} = \boxed{50\ ppm\ CaCO_3}$$

ii) pH from Ka_1 $HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$; $K_{eq} = \frac{[H_2CO_3][OH^-]}{[HCO_3^-]} = \frac{K_w}{Ka_1}$

$[alk]_T = 0.100\ \frac{mol\ H^+}{L}$

$T_{alk} = 5000\ ppm\ CaCO_3$

$0.100 - x$ x x

$\frac{x^2}{0.100 - x} = 2.22 \times 10^{-8}$ ← Solve for x using quadratic formula

So $x^2 + 2.22 \times 10^{-8} x - 2.22 \times 10^{-9} = 0$

$x = 4.7 \times 10^{-5}\ M = [OH^-]$ $\therefore pOH = 4.3$ & **pH = 9.7**

3. A water sample obtained from an area of dolimitic limestone ($CaCO_3.MgCO_3$) has a pH = 7.20 and a total alkalinity of 2.3×10^{-3} mol H^+ L^{-1}. Calculate the concentrations of all major ions in solution.

$$CaCO_3 \cdot MgCO_3 (s) \rightleftharpoons Ca^{2+} + Mg^{2+} + 2\,CO_3^{2-}$$

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

$[alk]_T \cong [HCO_3^-]$ at pH 7.20 (see pH speciation at pH 7.20)

Major ions in aqueous solution

Ca^{2+}, Mg^{2+}, HCO_3^-

where $[Ca^{2+}] = [Mg^{2+}]$ (same source)

Charge balance

$$2[Mg^{2+}] + 2[Ca^{2+}] = [HCO_3^-]$$

where $[HCO_3^-] = 2.3 \times 10^{-3} \frac{mol\ H^+}{L}$

$\therefore$ $4[Ca^{2+}] = 2.3 \times 10^{-3} \frac{mol}{L}$

$$[Ca^{2+}] = 5.8 \times 10^{-4} \frac{mol}{L}$$

$$[Mg^{2+}] = 5.8 \times 10^{-4} \frac{mol}{L}$$

$$[HCO_3^-] = 2.3 \times 10^{-3} \frac{mol}{L}$$