

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

$$[\text{alk}]_T = [\text{HCO}_3^-] + [\text{OH}^-] + 2[\text{CO}_3^{2-}] \quad \leftarrow \text{acid neutralizing capacity in mol H}^+/\text{L}$$

$$50. \frac{\text{mg CaCO}_3}{\text{kg}} \times \frac{1 \text{ mol}}{100.089} \times \frac{1 \text{ kg}}{1 \text{ L}} \times \frac{2 \text{ mol H}^+}{1 \text{ mol CaCO}_3} \times \frac{1 \text{ g}}{10^3 \text{ mg}} = 1.0 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

pH 7

$$[\text{OH}^-] = 10^{-7.0}$$

$[\text{CO}_3^{2-}]$ from K_{a2} expression, but negligible at pH 7; $[\text{CO}_3^{2-}] = \left(\frac{K_{a2}}{[\text{H}^+]}\right) [\text{HCO}_3^-]$

$$\therefore [\text{HCO}_3^-] = 1.0 \times 10^{-3} \text{ M}, \quad [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}, \quad [\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M}$$

pH 10

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

$$[\text{alk}]_T = [\text{HCO}_3^-] + [\text{OH}^-] + 2\left(\frac{K_{a2}}{[\text{H}^+]}\right) [\text{HCO}_3^-] = 1.0 \times 10^{-3} \text{ M}$$

$$[\text{HCO}_3^-] \left(1 + \frac{2K_{a2}}{[\text{H}^+]}\right) = 1.0 \times 10^{-3} - [\text{OH}^-]$$

$$[\text{HCO}_3^-] = 4.6 \times 10^{-4} \text{ M}, \quad [\text{CO}_3^{2-}] = 2.2 \times 10^{-4} \text{ M}, \quad [\text{OH}^-] = 1.0 \times 10^{-4} \text{ M}$$

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

i) $1.00 \times 10^{-3} \text{ M NaOH}$

ii) 0.100 M NaHCO_3

i) **pH = 11.0**

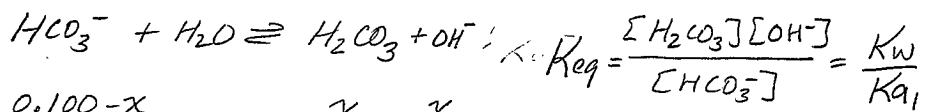
$$[\text{alk}]_T = 1.0 \times 10^{-3} \frac{\text{mol H}^+}{\text{L}}$$

$$T_{\text{alk}} = 1.0 \times 10^{-3} \frac{\text{mol H}^+}{\text{L}} \times \frac{100.089 \text{ g}}{1 \text{ mol CaCO}_3} \times \frac{1 \text{ mol CaCO}_3}{2 \text{ mol H}^+} \times \frac{10^3 \text{ mg}}{1 \text{ g}} = \boxed{50 \text{ ppm CaCO}_3}$$

ii) pH from K_{a1}

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

$$T_{\text{alk}} = \boxed{5000 \text{ ppm CaCO}_3}$$



$$0.100 - x \quad \quad \quad x \quad \quad x$$

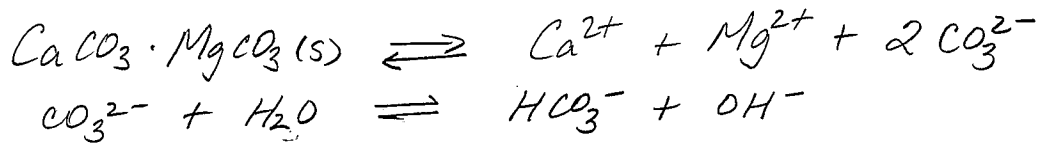
$$\frac{x^2}{0.100 - x} = 2.22 \times 10^{-8}$$

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

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

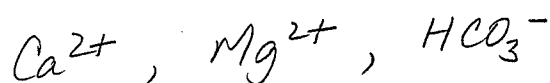
Solve for x using quadratic formula

3. A water sample obtained from an area of dolimitic limestone ($\text{CaCO}_3 \cdot \text{MgCO}_3$) has a $\text{pH} = 7.20$ and a total alkalinity of $2.3 \times 10^{-3} \text{ mol} \cdot \text{H}^+ \text{ L}^{-1}$. Calculate the concentrations of all major ions in solution.



$$[\text{alk}]_T \cong [\text{HCO}_3^-] \quad \text{at pH } 7.20 \quad (\text{see pH speciation at pH } 7.20)$$

Major ions in aqueous solution



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

Charge balance

$$2[\text{Mg}^{2+}] + 2[\text{Ca}^{2+}] = [\text{HCO}_3^-]$$

$$\text{where } [\text{HCO}_3^-] = 2.3 \times 10^{-3} \frac{\text{mol H}^+}{\text{L}}$$

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

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

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

$$[\text{HCO}_3^-] = 2.3 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$