Calculation of Bicarbonate, Carbonate and Hydroxide Alkalinity

1. remember, total alkalinity is the amount of acid required to lower the pH of the solution to 4.5

2. can be divided into various species if inflection points are known

   a. phenolphthalein alkalinity (hydroxide and ½ carbonate neutralized) occurs when sufficient acid has been added to lower pH to 8.3 -- solution goes pink

      i. carbonate actually converted to bicarbonate (by pH 7)

   b. additional acid to reduce pH 8.3 to 4.5 neutralizes remaining ½ carbonate (already converted to bicarbonate) and the bicarbonate -- solution turns orange

(a) carbonate alkalinity is present when the phenolphthalein alkalinity is not zero, but less than the total alkalinity

(b) Hydroxide alkalinity is present if the phenolphthalein alkalinity is more than half the total alkalinity

(c) Bicarbonate alkalinity is present if the phenolphthalein alkalinity is less than half the total alkalinity

(d) Bicarbonate and Hydroxide alkalinities cannot be present together

(e) All hydroxide alkalinity is neutralized by pH 10.0

(f) all Carbonates are converted to bicarbonates by pH 8.3

Group	Result of Titration	Hydroxide Alkalinity	Carbonate Alkalinity	Bicarbonate Alkalinity
A	P = 0	0	0	T (initial pH < 8.3)
B	P = 0.5T	0	2P	0
C	P = T	T	0	0
D	P < 0.5T	0	2P	T-2P
E	P > 0.5T	2P - T	2(T-P)	0

where

P = amount of acid required to reach 8.3

T = total amount of acid required to reach 4.5

Common convention in Environmental Engineering is the use of $CaCO_3$ equivalent to express chemical concentration in mg/L, (Benefield, Judkins and Weand, 1982 *Process Chemistry for Water and Wastewater Treatment*, pg. 10) **As it Allows Addition**

where

$$mg/L \ as \ CaCO_3 = [mg/L \ of \ Substance] \left[\frac{MWT \ of \ CaCO_3}{MWT \ of \ Substance} \right]$$

thus P = Phenolphthalein alkalinity as $CaCO_3$ in mg/L
T = Total alkalinity as $CaCO_3$ in mg/L

Controversy

1. confusion exists with $CaCO_3$ as it does not always have an equivalent weight of 50 mg/meq (Snoeynik and Jenkins, 1980 *Water Chemistry*) when converting eq/m^3 to mg/L

2. reason is that occasionally $CaCO_3$ has a valence of 1 instead of 2 giving it a mg/meq of 100; best to use mg/L. **Important for Subsequent Hardness Calculations**

3. Example

$$CaCO_3 \rightarrow Ca^{2+} + CO_3^{2-}$$

1 mole $CaCO_3$ yields 1 mole, or 2 equivalents of Ca^{2+} & CO_3^{2-}

$\therefore$ equivalent weight as $CaCO_3$

$$= \frac{100 \ g/mole}{2 \ eq/mole} = 50 \ g/eq$$

same goes for Mg^{2+} as it is divalent, $\therefore$ $CaCO_3$ equivalent for Mg^{2+} = 50 g/eq

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$$C_aCO_3 + H^+ \rightarrow C_a^{2+} + HCO_3^-$$

here equivalent weight

$$= \frac{100 \ g/mole}{1 \ eq/mole} = 100 g/eq \qquad for \ HCO_3^-$$