Department of Civil Engineering-I.I.T. Delhi

CEL 212: Environmental Engineering

Second Semester 2012-13

Home Work 2: Alkalinity and Hardness (updated)

Q1. A 200-mL sample of water has initial pH 10. Thirty milliliters of 0.025 N sulfuric acid is required to titrate the sample to pH 6. What are total alkalinity, carbonate, bicarbonate and hydroxide alkalinity? Define carbonate hardness?

Answer:

pH 10 => All three types of alkalinity; pOH=14-pH = 14-10=4; [OH-] $=10^{-pOH} = 10^{-4}$ moles/L

Number of hydroxide equivalents = (17g/mole*10^{-4} mole/L)/(17g/equivalent) = 10^{-4} equivalents/L = number of equivalents of $CaCO_3$

Hydroxide alkalinity = (equivalent weight of $CaCO_3$ =50 g/equivalent)*(10^{-5} equivalents of $CaCO_3$/L) $=50*10^{-5}*10^{3}$ = **0.5 mg/L $CaCO_3$**

As titration was done using 0.025N H_2SO_4 and titration was done till pH 6 where 30 mL sulfuric acid is consumed. It indicates that sample has hydroxide alkalinity, carbonate and bicarbonate alkalinities, if we assume that titration

The distribution of carbonate and bicarbonate alkalinities depend on concentration of carbonate and bicarbonate concentrations at pH 6 and it depends on equilibrium between carbonate and bicarbonate species.

The equilibrium equations which must be considered are that for water [Eq. (17-6)] and that for the second ionization of carbonic acid,

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_{A2} \qquad (17\text{-}11)$$

From a pH measurement, $[H^+]$ and $[OH^-]$ can be determined, using Eq. (17-6). The only other unknowns are $[HCO_3^-]$ and $[CO_3^{2-}]$, and these can be determined from a simultaneous solution of Eqs. (17-10) and (17-11). The following equations result:

$$\text{Carbonate alkalinity (mg/l as } CaCO_3) = \frac{50{,}000[(\text{alkalinity}/50{,}000) + [H^+] - (K_W/[H^+])]}{1 + ([H^+]/2K_{A2})} \qquad (17\text{-}12)$$

$$\text{Bicarbonate alkalinity (mg/l as } CaCO_3) = \frac{50{,}000[(\text{alkalinity}/50{,}000) + [H^+] - (K_W/[H^+])]}{1 + (2K_{A2}/[H^+])} \qquad (17\text{-}13)$$

At 25°C, K_W is 10^{-14} and K_{A2} is 4.7×10^{-11}. However, these values vary quite radically with temperature. Also, the activities of the ions vary considerably with ionic concentration, as indicated in Sec. 4-3. These corrections are rather tedious; consequently, "Standard Methods" presents nomographs for the ... of carbonate and bicarbonate based on these considerations. The

Now we calculate alkalinity till pH 6.

Amount of sulfuric acid consumed = (30/1000)(L)*(0.025)/(0.2L sample) =0.00375 equivalents/L

[Alkalinity in terms of mass of $CaCO_3$ in g/L]/ (50/equivalents) = (0.00375)

[Alkalinity in terms of Mass of $CaCO_3$ in mg/L]= (50)*(0.00375)*1000 mg/L =187.5mg/L as $CaCO_3$

$Kw=[H^+][OH^-]$
$[H^+] =(10^{-6})$
$[OH^-] = Kw/[H^+] =(10^{-14})/(10^{-6}) = (10^{-8})$

say (A) = 50000 *{(alkalinity/50000)+$[H^+]$-$[OH^-]$}
=50000 *{(187.5 mg/L as $CaCO_3$/50000)+ (10^{-6}) -(10^{-8})}=(187.5)+[0.0495]
A=187.55 mg/L as $CaCO_3$

carbonate alkalinity (mg/L as $CaCO_3$) = A/[1+ {$[H^+]$/(2*Ka)}]
=(187.55)/[1+ {$[10^{-6}]$/(2*4.7*10^{-11})}]
carbonate alkalinity =0.0176 mg/L as $CaCO_3$

bicarbonate alkalinity (mg/L as $CaCO_3$) = A/[1+ {(2*Ka)/ $[H^+]$}]
=(187.55)/[1+ { (2*4.7*10^{-11})/ $[10^{-6}]$}]
bicarbonate alkalinity =187.53 mg/L as $CaCO_3$

Q2. During alkalinity determination for sample #2 (pH 9), my student used 50 mL of 0.02N H_2SO_4 till phenolphthalein end point and 100 mL total of same acid till bromocresol green end point from start of the titration, how much hydroxide, carbonate and bicarbonate alkalinities you would expect? <u>(6 points)</u>
Answer:
pH 9 => All three types of alkalinity
pOH=14-pH = 14-9=5
[OH-] =10^{-pOH} = 10^{-5} moles/L
Number of hydroxide equivalents = (17g/mole*10^{-5} mole/L)/(17g/equivalent) = 10^{-5} equivalents/L = number of equivalents of $CaCO_3$
Hydroxide alkalinity = (equivalent weight of $CaCO_3$ =50 g/equivalent)*(10^{-5} equivalents of $CaCO_3$/L)
=50*10^{-5}*10^3 = **0.5 mg/L $CaCO_3$**

As titration was done using 0.02N H_2SO_4, so phenolphthalein alkalinity = (X mL of 0.02N H_2SO_4) *(1000/sample volume in mL) mg/L $CaCO_3$
Assume 100 mL sample volume:
So, phenolphthalein alkalinity = (50)*(1000/100)= 500 mg/L $CaCO_3$
Similarly, total alkalinity = (100)*(1000/100)= 1000 mg/L $CaCO_3$

Carbonate alkalinity = 2*[Phenolphthalein alkalinity-hydroxide alkalinity]
=2*[500-0.5]=2*[499.5]**=999 mg/L $CaCO_3$**

Bicarbonate alkalinity = Total alkalinity -[Carbonate alkalinity + hydroxide alkalinity]
=1000-[999+0.5]=**0.5 mg/L $CaCO_3$**

Q3. How does algal growth in lake helps in maintaining buffering capacity of a lake system? What would happen if I inject carbon dioxide captured from coal-powered plants into this lake?
Answer:
Algae consume carbon dioxide in presence of sunlight and produce new algal cells and oxygen.However in the absence of light, algae consumes oxygen to produce carbon dioxide. It results in diurnal variation in CO2 concentration in water and thus it affects alkalinity of the system (and thus the buffering capacity of the system).

For high algae growth pH changes to 10 due to above consideration. With increase in pH, forms of alkalinity changes and CO2 can also be extracted for algal growth both from carbonates and biocarbonates as per following equation:

$$2HCO_3^- \Leftrightarrow CO_3^{2-} + H_2O + CO_2$$
$$CO_3^{2-} + H_2O \Leftrightarrow 2OH^- + CO_2$$

thus the removal of CO2 by algae tends to cause a shift in forms of alkalinity present from bicarbonate to carbonate and form carbonate to hydroxide. **However in this process, alkalinity remains constant.**
(see notes below also)

Q4. My student collected a raw wastewater sample from a community "AA" and reported me the presence of nitrogen and organic carbon in the sample using ammonia and TOC analysis (solution pH=5). To determine BOD of the sample, what type(s) of BOD she should consider and how are they related to each other? Also, what types of alkalinity you would expect in this sample? **(6 points)**

Answer

As sample has organic carbon and nitrogen (from ammonia), one would expect both carbon-based and nitrogen-based BOD values.

As pH=5, one would expect hydroxide, carbonate and bicarbonate alkalinity. The order would be: bicarbonate alkalinity > carbonate alkalinity > hydroxide alkalinity.

Q5. A water has the following analysis:

Ion type	Concentration (mg/L)	Ion type	Concentration (mg/L)
Na^+	20	Cl^-	40
Ca^{2+}	5	CO_3^{2-}	10
Mg^{2+}	10	SO_4^{2-}	5

Calculate values of total hardness and non-carbonate hardness in mg/L as $CaCO_3$?

Answer:

Only cations with bivalency contribute to hardness.

Hardness (in mg/L) as $CaCO_3$ = M^{2+} (in mg/L) *[(50)/(Equivalent weight of M^{2+})]

Cation	Concentration (mg/L)	Equivalent weight (g/mole)	Hardness (in mg/L) as $CaCO_3$
Ca^{2+}	5	20	=(5) *[(50)/(20)]=12.5
Mg^{2+}	10	12.2	=(10) *[(50)/(12.2)]=41

Total hardness = Hardness due to Ca^{2+} ions and Mg^{2+} ions. = 12.5+41=**53.5 mg/L as $CaCO_3$ (answer)**

For calculating non-carbonate hardness:

Anion	Concentration (mg/L)	Equivalent weight (g/mole)	Hardness (in mg/L) as $CaCO_3$
CO_3^{2-}	10	=(12+3*16)/2= 30	=(10) *[(50)/(30)]=16.67

As the maximum value of carbonate hardness could be 16.67 mg/L as $CaCO_3$ and given that total hardness is 53.5 mg/L as $CaCO_3$, this non-carbonate hardness (minimum value)

= 53.5-16.67 =**36.83 mg/L as $CaCO_3$**