375 Assignment 2

(1)

step 1: convert concentration g/m³ into eq/mol

example HCO_3^- MW = 61.01 g/mol Z = 1 eq/mol

in sample 2, HCO_3^- = 156.9 g/m³

$$\frac{156.9\ g}{m^3} \left| \frac{mol}{61.01\ g} \right| \frac{1\ eq}{mol} = 2.57\ eq/m^3$$

step 2: Anion - Cation Balance

$$|\Sigma \text{anions}| = |\Sigma \text{cations}|$$

∴ sample 1: $SO_4^{2-} \approx 8.88\ eq/m^3$

$= 426.5\ g/m^3$

sample 2: $Cl^- \approx 0\ eq/m^3$

$= 0\ g/m^3$

See Attached Excel Table

(2) Express 36.2 mg/L of Ca^{2+} as

a) mg/L $CaCO_3$ MW = 100 g/mol Z = 2.

convert to eq/L

$$\frac{36.2\ mg}{L} \left| \frac{g}{1000\ mg} \right| \frac{mol}{40\ g} \left| \frac{2\ eq}{mol} \right| = 1.81 \times 10^{-3}\ eq/L$$

convert back to mg/L as $CaCO_3$

$$\frac{1.81 \times 10^{-3}\ eq}{L} \left| \frac{mol}{2\ eq} \right| \frac{100\ g}{mol} \left| \frac{1000\ mg}{g} \right| = 90.5\ mg/L \text{ as } CaCO_3$$

b) ppm as $CaCO_3$

- Assume specific gravity of solvent (water) = 1

$$ppm = \frac{\text{concentration g/m}^3}{\text{spec. grav. of solvent}}$$

∴ mg/L = g/m³ = ppm = 90.5 ppm as $CaCO_3$

(2) c) meq/L as $CaCO_3$

Recall from a) 1.81×10^{-3} eq/L as $CaCO_3$

$= 1.81$ meq/L as $CaCO_3$

(3) Calculate pH

a) 8.27×10^{-9} mol/L of H^+

$$pH = -\log[H^+] = 8.08$$

b) 4.32×10^{-6} mol/L of OH^-

$$pH = 14 + \log[OH^-] = 8.64$$

c) 87 mg/L of OH^- MW = 17g/mol

$$\frac{87 \text{ mg}}{\text{L}} \left| \frac{\text{g}}{1000 \text{ mg}} \right| \frac{\text{mol}}{17 \text{ g}} = 5.12 \times 10^{-3} \text{ mol/L}$$

$$pH = 14 + \log[OH^-] = 11.71$$

(4) comment ons

i) pH = 7.8 ~ slightly basic
ii) Hardness.

Ions present that cause hardness: $Ca^{2+} + Mg^{2+}$

$$\text{Total Hardness} = \Sigma \frac{M^{2+}(\text{mg/L}) \times 50^{\text{g}}/\text{meq } CaCO_3}{EW \text{ of } M^{2+}}$$

$$= \left(\frac{[Ca^{2+}]}{EW\, Ca^{2+}} + \frac{[Mg^{2+}]}{EW\, Mg^{2+}} \right) \times 50 \text{ mg/meq } CaCO_3$$

$$= \left[\frac{42 \text{ mg/L}}{20.04 \text{ g/eq}} + \frac{19 \text{ mg/L}}{12.15 \text{ g/eq}} \right] \times 50 \text{ g/eq } CaCO_3$$

$= 183.0$ mg/L as $CaCO_3 \approx$ Hard
look at table p 3-8 in notes

④ iii) Electroneutrality of solution

see excel table

Σ anions $\neq \Sigma$ cations.

∴ Analysis not complete.

⑤ $K_{sp} = 2\times10^{-5}$ how much $CaSO_4$ can be dissolved

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

- Assume pure water as the solvent
- Since 1 mole $CaSO_4$ yeilds 1 mole of Ca^{2+} and 1 mole SO_4^{2-}, then

$$[Ca^{2+}] = [SO_4^{2-}]$$

$$\therefore K_{sp} = [Ca^{2+}]^2 \rightarrow [Ca^{2+}] = [SO_4^{2-}] = \sqrt{2\times10^{-5}} = 4.47\times10^{-3} \text{ mol/L}$$

for Ca^{2+}, $\frac{4.47\times10^{-3}\text{ mol}}{\text{L}} \left| \frac{40.01\text{ g}}{\text{mol}} \right| \frac{1000\text{ mg}}{\text{g}} = 178.8 \text{ mg/L}$

SO_4^{2-} $\frac{4.47\times10^{-3}\text{ mol}}{\text{L}} \left| \frac{96.06\text{ g}}{\text{mol}} \right| \frac{1000\text{ mg}}{\text{g}} = 429.4 \text{ mg/L}$

⑥ $(CO_3^{2-}) = 0.6\times10^{-2}$ mg/L $\quad K_{sp} = 5.0\times10^{-9}$

i) $\frac{0.6\times10^{-2}\text{ mg}}{\text{L}} \left| \frac{\text{mol}}{60\text{ g}} \right| \frac{\text{g}}{1000\text{ mg}} = 10^{-7} \text{ mol/L}$

$$CaCO_3(s) \rightleftharpoons Ca^{2+} + CO_3^{2-}$$

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] \rightarrow [Ca^{2+}] = \frac{5.0\times10^{-9}}{10^{-7}} = 0.05 \text{ mol/L}$$

$$(Ca^{2+}) = \frac{0.05\text{ mol}}{\text{L}} \left| \frac{40.01\text{ g}}{\text{mol}} \right| \frac{1000\text{ mg}}{\text{g}} = 2.0\times10^{3} \text{ mg/L}$$

cont'd

(6) ii) $Na_2CO_3(s) \rightleftharpoons 2Na^+ + CO_3^{2-}$

Assume complete dissociation

$[CO_3^{-2}] = 1.6\times10^{-5}$ mol/L

$$[Ca^{2+}] = \frac{K_{sp}}{[CO_3^{2-}]} = \frac{5\times10^{-9}}{1.6\times10^{-5}} = 3.125\times10^{-4}$$

$$(Ca^{2+}) = \frac{3.125\times10^{-4}\ \text{mol}}{L} \left| \frac{40.0\text{g}}{\text{mol}} \right| \frac{1000\text{mg}}{\text{g}}$$

$= 12.5$ mg/L

- the addition of Na_2CO_3 added more CO_3^{2-} into the system. An excess of CO_3^{2-} will react with Ca^{2+} in the system and precipitate as $CaCO_3$, thus reducing the overall concentration of Ca^{2+}.

(7) $MgCO_3 \rightleftharpoons Mg^{2+} + CO_3^{2-}$ $\quad K_{sp} = 4\times10^{-5}$

- Assume complete dissociation

Since 1 mole $MgCO_3$ yields 1 mole of both Mg^{2+} and CO_3^{2-}, then we can say that

$[Mg^{2+}] = [CO_3^{2-}]$ $\quad \therefore$ let x = conc. of $[Mg^{2+}]$ and $[CO_3^{2-}]$

$\therefore K_{sp} = [Mg^{2+}][CO_3^{2-}] = x^2$ $\quad$ so $x = 6.325\times10^{-3}$ mol/L

but we are adding 2.2×10^{-3} mol/L of Mg^{2+}.
Thus we rewrite the equation as:

$$K_{sp} = \underbrace{(x+2.2\times10^{-3})}_{\text{new conc of } Mg^{2+}}\underbrace{(x)}_{\text{conc. of } CO_3^{2-}}$$

recall quadratic $\quad x = \dfrac{-b \pm \sqrt{b^2-4ac}}{2a}$

solve $0 = x^2 + 2.2\times10^{-3}x - 4\times10^{-5}$

$x = 5.32\times10^{-3}$ and ~~-7.52×10^{-3}~~ cannot have negative concentration

cont'd ↓

(7) Now, $x = 5.32\times10^{-3}$ mol/L

$[Mg^{2+}] = x + 2.2\times10^{-3} = 7.52\times10^{-3}$ mol/L

$[CO_3^{2-}] = x = 5.32\times10^{-3}$ mol/L

How much $MgCO_3$ precipitated after adding the 2.2×10^{-3} mol/L Mg^{2+}?

lets look at the change in $[CO_3^{2-}]$

initially $[CO_3^{2-}] = 6.325\times10^{-3}$ mol/L

after addition of Mg^{2+} $[CO_3^{2-}] = 5.32\times10^{-3}$ mol/L

difference $= 1.005\times10^{-3}$ mol/L

∴ 1.005×10^{-3} mol/L $MgCO_3$ precipitated after add 2.2×10^{-3} mol/L Mg^{2+}

(8) 100 mg HCl added to 1.0L of water

$HCl(s) \rightleftharpoons H^+ + Cl^-$

How many moles equals 100 mg HCl

$MW_{HCl} = 36.46$ g/mol → $\frac{\text{mol}}{36.46\text{g}} \left| \frac{100\text{mg}}{} \right| \frac{\text{g}}{1000\text{mg}} = 2.74\times10^{-3}$ mol

a) $pH = -\log[H^+] = -\log(2.74\times10^{-3}) = 2.56$

b) $pH = 7 = -\log(2.74\times10^{-3} + x)$

$x = 10^{-7} - 2.74\times10^{-3}$

$= -2.7399\times10^{-3}$

∴ we need to reduce $[H^+]$ by adding $[OH^-]$

$H^+ + OH^- \rightleftharpoons H_2O$

cont'd ↓

(8) cont'd

by adding NaOH, we need to get 2.7399×10^{-3} moles of OH^- to get pH = 7

$$NaOH_{(s)} \rightleftharpoons Na^+_{(aq)} + OH^-_{(aq)}$$

$MW_{NaOH} = 40\ g/mol$

$$\frac{40\ g}{mol} \;\Big|\; 2.7399 \times 10^{-3}\ mol \;\Big|\; \frac{1000\ mg}{g}$$

$\therefore$ 109.6 mg of NaOH must be added to get a pH of 7.0.

(9) Look Notes Page 3-22

Governing Equations $\quad HA \rightleftharpoons H^+ + A^-$

① $K_w = 10^{-14} = [H^+][OH^-]$

② $K_a = 2.47 \times 10^{-7} = \dfrac{[H^+][A^-]}{[HA]}$

③ $C_T = 5 \times 10^{-6} = [HA] + [A^-]$

④ $[H^+] = [OH^-] + [A^-]$

4 equations, 4 unknowns: $[H^+]$ $[OH^-]$ $[HA]$ $[A^-]$

Solve For $[H^+]$

Assume $[H^+] \gg [OH^-]$ since we're adding an acid

From ④ $\quad [H^+] = [A^-]$

From ② $\quad [HA] = \dfrac{[H^+]^2}{2.47 \times 10^{-7}}$

sub in ③ $\quad 5 \times 10^{-6} = \dfrac{[H^+]^2}{2.47 \times 10^{-7}} + [H^+]$

$\therefore [H^+] = 9.95 \times 10^{-7}$ and ~~-1.24×10^{-6}~~

$\therefore pH = -\log(9.95 \times 10^{-7}) = 6.0$

check Assumption $\quad [OH^-] = \dfrac{10^{-14}}{[H^+]} = 10^{-8} \ll [H^+]$ O.K.

(10) Find pH + concentrations $K_A = 1.8\times10^{-5}$

a) $H(CH_3COO) \rightleftharpoons H^+ \; CH_3COO^-$ $C_T = 2.5\times10^{-3}$ M

using equations: ① $10^{-14} = [H^+][OH^-]$

② $\dfrac{[H^+][CH_3COO^-]}{[H(CH_3COO)]} = 1.8\times10^{-5}$

③ $[CH_3COO^-] + [H(CH_3COO)] = 2.5\times10^{-3}$

④ $[H^+] = [OH^-] + [CH_3COO^-]$

Again, Assume $[H^+] \gg [OH^-]$

$\therefore [H^+] = [CH_3COO^-]$

Solve for $[H^+]$, just like question (9)

$[H^+] = 2.033\times10^{-4}$ mol/L

pH = 3.69

$[CH_3COO^-] = 2.033\times10^{-4}$ mol/L

$[OH^-] = 4.919\times10^{-11}$ mol/L

$[H(CH_3COO)] = 2.3\times10^{-3}$ mol/L

$[H^+] \gg [OH^-]$

$\therefore$ Assumption O.K.

b) 2.5×10^{-3} M $Na(CH_3COO^-)$ assume complete dissociation

$\therefore Na(CH_3COO^-) \rightarrow Na^+ + CH_3COO^-$

$\therefore [Na(CH_3COO)] = [Na^+] = 2.5\times10^{-3}$ mol/L

but CH_3COO will accept H^+ from the water

$H_2O + CH_3COO^- \rightleftharpoons H(CH_3COO) + OH^-$

this reaction creates extra OH^-, thus causing water to become basic

$\therefore$ Assume $[OH^-] \gg [H^+]$

$K_B = \dfrac{K_W}{K_A} = \dfrac{10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$

cont'd ↓

(10) governing equations:

① $[H^+][OH^-] = 10^{-14}$

② $\frac{[OH^-][H(CH_3COO)]}{[H_2O][CH_3COO^-]} = K_B = 5.56\times10^{-10}$ (Pg 3-20 in notes)

③ $C_T = [CH_3COO^-] + [H(CH_3COO)] = 2.5\times10^{-3}$

④ $[Na^+] + [H^+] = [OH^-] + [CH_3COO^-]$ (Electroneutrality equation)

⑤ $[Na^+] = 2.5\times10^{-3}$ mol/L.

solve for $[OH^-]$, remember $[OH^-] >> [H^+]$

rearrange ④: $[CH_3COO^-] = 2.5\times10^{-3} - [OH^-]$

sub into ③: $[H(CH_3COO)] = [OH^-]$

sub into ②: $[OH^-]^2 = 5.56\times10^{-10}(2.5\times10^{-3} - [OH^-])$

$\therefore [OH^-] = 1.18\times10^{-6}$ mol/L

$pH = 8.07$

$[H^+] = 8.51\times10^{-9}$ mol/L

$[OH^-] >> [H^+]$ ∴ Assump. O.K.

$[H(CH_3COO)] = 1.18\times10^{-6}$ mol/L

$[CH_3COO^-] = 2.5\times10^{-3}$ mol/L

$[Na^+] = 2.5\times10^{-3}$ mol/L

(II) a) see Excel sheet

Σ cations $\approx$ Σ Anions

$\therefore$ Analysis is reasonable

b) Hardness ions present Ca^{2+}, Mg^{2+}, Fe^{2+}, Cd^{2+}

$$\text{Total Hardness} = \left[\frac{[Ca^{2+}]}{EW_{Ca^{2+}}} + \frac{[Mg^{2+}]}{EW_{Mg^{2+}}} + \frac{[Fe^{2+}]}{EW_{Fe^{2+}}} + \frac{[Cd^{2+}]}{EW_{Cd^{2+}}}\right] \times 50\ g/eq\ CaCO_3$$

$= 821.0\ g/m^3$ as $CaCO_3$ (water is very hard)
p. 3-8 in notes

NOTE do part d) first

d) $[HCO_3^-] = 260\ g/m^3 = 4.75\times10^{-3}\ mol/L$

$pHCO_3^- = -\log(4.75\times10^{-3}) = 2.32$

$[CO_3^{2-}] = 30\ g/m^3 = 5.0\times10^{-4}\ mol/L$

$pCO_3^{2-} = 3.3.$

looking at Figure 4 from Lab 1 on page 9, we find $pH \approx 9.5$

back to c)

c) $Alk = [HCO_3^- + CO_3^{2-} + OH^- - H^+\ eq/L] \times 50\ g/eq$

p. 3-10 in Notes

$= [4.26\times10^{-3} + 1\times10^{-3} + 3.16\times10^{-5} - 3.16\times10^{-10}]$

$= 5.26\times10^{-3}\ eq/L \times 50\ g/eq \times 1000\ L/m^3$

Note since $pH > 8.3$, we use $50\ g/eq$ for $CaCO_3$

$\therefore$ $Alk = 264.5\ g/m^3$ as $CaCO_3$

e) since pH is very high, water is very hard and $[Cd^{2+}] > 0.01\ g/m^3$, water would not be acceptable for domestic supply.