

375 Assignment 2

①

step 1: convert concentration g/m^3 into eq/mol

example HCO_3^- MW = 61.01 g/mol $Z = 1 \text{ eq/mol}$

in sample 2, $\text{HCO}_3^- = 156.9 \text{ g/m}^3$

$$\frac{156.9 \text{ g}}{\text{m}^3} \times \frac{\text{mol}}{61.01 \text{ g}} \times \frac{1 \text{ eq}}{\text{mol}} = 2.57 \text{ eq/m}^3$$

step 2: Anion - Cation Balance

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

$$\therefore \text{sample 1: } \text{SO}_4^{2-} \approx 8.88 \text{ eq/m}^3 \\ = 426.5 \text{ g/m}^3$$

$$\text{sample 2: } \text{Cl}^- \approx 0 \text{ eq/m}^3 \\ = 0 \text{ g/m}^3$$

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
convert back
to mg/L as CaCO_3

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

$$\frac{1.81 \times 10^{-3} \text{ eq}}{\text{L}} \times \frac{\text{mol}}{2 \text{ eq}} \times \frac{100 \text{ g}}{\text{mol}} \times \frac{1000 \text{ mg}}{\text{g}} = 90.5 \text{ mg/L as } \text{CaCO}_3$$

b) ppm as CaCO_3

- Assume specific gravity of solvent (water) = 1

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

$$\therefore \text{mg/L} = \text{g/m}^3 = \text{ppm} = 90.5 \text{ ppm as } \text{CaCO}_3$$

② c) mg/L as CaCO_3

Recall from d) $1.81 \times 10^{-3} \text{ eq/L}$ as CaCO_3
 $= 1.81 \text{ meq/L}$ as CaCO_3

③ Calculate pH

a) $8.27 \times 10^{-2} \text{ mol/L}$ of H^+

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

b) $4.32 \times 10^{-6} \text{ mol/L}$ of OH^-

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

c) 87 mg/L of OH^- $\text{MW} = 17 \text{ g/mol}$

$$\frac{87 \text{ mg}}{\text{L}} \times \frac{1 \text{ g}}{1000 \text{ mg}} \times \frac{1 \text{ mol}}{17 \text{ g}} = 5.12 \times 10^{-3} \text{ mol/L}$$

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

④ comment on:

- i) $\text{pH} = 7.8$ ~ slightly basic
- ii) Hardness.

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

$$\begin{aligned} \text{Total Hardness} &= \sum \frac{\text{M}^{2+} (\text{mg/L}) \times 50 \text{ g/meq CaCO}_3}{\text{EW of M}^{2+}} \\ &= \left(\frac{[\text{Ca}^{2+}]}{\text{EW Ca}^{2+}} + \frac{[\text{Mg}^{2+}]}{\text{EW Mg}^{2+}} \right) \times 50 \text{ mg/meq CaCO}_3 \\ &= \left[\frac{42 \text{ mg/L}}{20.04 \text{ g/eq}} + \frac{19 \text{ mg/L}}{12.15 \text{ g/eq}} \right] \times 50 \text{ g/eq CaCO}_3 \\ &= 183.0 \text{ mg/L as CaCO}_3 \approx \text{Hard} \end{aligned}$$

look at table p 3-8 in notes

④ iii) Electroneutrality of solution
see excel table

2 anions $\neq$ 2 cations.
 $\therefore$ Analysis not complete.

⑤ $K_{sp} = 2 \times 10^{-5}$ how much CaSO_4 can be dissolved



$$K_{sp} = [\text{Ca}^{2+}][\text{SO}_4^{2-}]$$

- Assume pure water as the solvent

- Since 1 mole CaSO_4 yields 1 mole of Ca^{2+}
and 1 mole SO_4^{2-} , then

$$[\text{Ca}^{2+}] = [\text{SO}_4^{2-}]$$

$$\therefore K_{sp} = [\text{Ca}^{2+}]^2 \Rightarrow [\text{Ca}^{2+}] = [\text{SO}_4^{2-}] = \sqrt{2 \times 10^{-5}} = 4.47 \times 10^{-3} \text{ mol/L}$$

$$\text{For } \text{Ca}^{2+}, \frac{4.47 \times 10^{-3} \text{ mol}}{\text{L}} \left| \frac{40.01 \text{ g}}{\text{mol}} \right| \frac{1000 \text{ mg}}{\text{g}} = 178.8 \text{ mg/L}$$

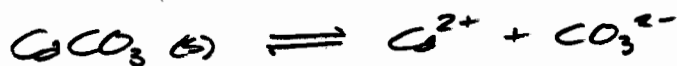
$$\text{SO}_4^{2-} \frac{4.47 \times 10^{-3} \text{ mol}}{\text{L}} \left| \frac{96.06 \text{ g}}{\text{mol}} \right| \frac{1000 \text{ mg}}{\text{g}} = 429.4 \text{ mg/L}$$

⑥

$$(\text{CO}_3^{2-}) = 0.6 \times 10^{-2} \text{ mg/L}$$

$$K_{sp} = 5.0 \times 10^{-9}$$

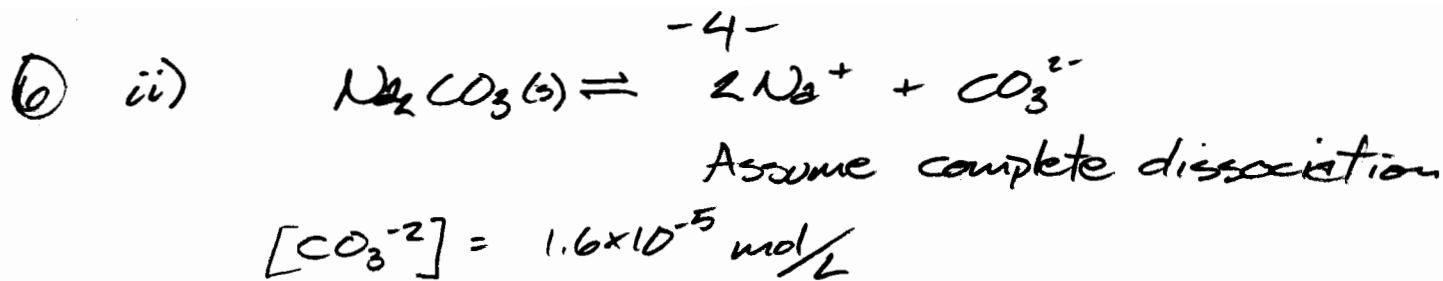
$$i) \frac{0.6 \times 10^{-2} \text{ mg}}{\text{L}} \left| \frac{\text{mol}}{60 \text{ g}} \right| \frac{\text{g}}{1000 \text{ mg}} = 10^{-7} \text{ mol/L}$$



$$K_{sp} = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \Rightarrow [\text{Ca}^{2+}] = \frac{5.0 \times 10^{-9}}{10^{-7}} = 0.05 \text{ mol/L}$$

$$(\text{Ca}^{2+}) = \frac{0.05 \text{ mol}}{\text{L}} \left| \frac{40.01 \text{ g}}{\text{mol}} \right| \frac{1000 \text{ mg}}{\text{g}} = 2.0 \times 10^3 \text{ mg/L}$$

✓ correct

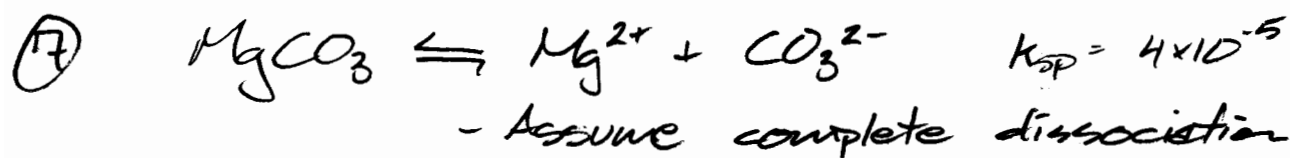


$$[\text{Ca}^{2+}] = \frac{K_{sp}}{[\text{CO}_3^{2-}]} = \frac{5 \times 10^{-9}}{1.6 \times 10^{-5}} = 3.125 \times 10^{-4}$$

$$(\text{Ca}^{2+}) = \frac{3.125 \times 10^{-4} \text{ mol}}{\text{L}} \quad \left| \quad \frac{40.01 \text{ g}}{\text{mol}} \quad \right| \quad \frac{1000 \text{ mg}}{\text{g}}$$

$$= 12.5 \text{ mg/L}$$

- 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+} .



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

$$[\text{Mg}^{2+}] = [\text{CO}_3^{2-}] \quad \therefore \text{let } x = \text{conc. of } [\text{Mg}^{2+}] \text{ and } [\text{CO}_3^{2-}]$$

$$\therefore K_{sp} = [\text{Mg}^{2+}][\text{CO}_3^{2-}] = x^2 \quad \text{so } x = 6.325 \times 10^{-3} \text{ mol/L}$$

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

$$K_{sp} = \underbrace{(x + 2.2 \times 10^{-3})}_{\text{new conc of } \text{Mg}^{2+}} \underbrace{(x)}_{\text{conc. of } \text{CO}_3^{2-}}$$

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

solve $0 = x^2 + 2.2 \times 10^{-3}x - 4 \times 10^{-5}$

↓ cont'd

$$x = 5.32 \times 10^{-3} \text{ and } -7.52 \times 10^{-3}$$

cannot have negative concentration

-5-

⑦

Now, $x = 5.32 \times 10^{-3} \text{ mol/L}$

$$[\text{Mg}^{2+}] = x + 2.2 \times 10^{-3} = 7.52 \times 10^{-3} \text{ mol/L}$$

$$[\text{CO}_3^{2-}] = x = 5.32 \times 10^{-3} \text{ mol/L}$$

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

lets look at the change in $[\text{CO}_3^{2-}]$

initially $[\text{CO}_3^{2-}] = 6.325 \times 10^{-3} \text{ mol/L}$

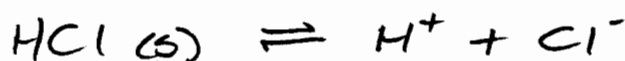
after addition of Mg^{2+} $[\text{CO}_3^{2-}] = 5.32 \times 10^{-3} \text{ mol/L}$

difference = $1.005 \times 10^{-3} \text{ mol/L}$

$\therefore 1.005 \times 10^{-3} \text{ mol/L}$ MgCO_3 precipitated after add $2.2 \times 10^{-3} \text{ mol/L}$ Mg^{2+}

⑧

100 mg HCl added to 1.0L of water



How many mols equals 100 mg HCl

$$\text{MW}_{\text{HCl}} = 36.46 \text{ g/mol} \rightarrow \frac{\text{mol}}{36.46 \text{ g}} \left| \frac{100 \text{ mg}}{1000 \text{ mg}} \right| \frac{\text{g}}{\text{g}} = 2.74 \times 10^{-3} \text{ mol}$$

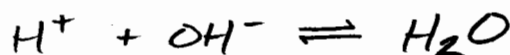
a) $\text{pH} = -\log[\text{H}^+] = -\log(2.74 \times 10^{-3}) = 2.56$

b) $\text{pH} = 7 = -\log(2.74 \times 10^{-3} + x)$

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

$$= -2.7399 \times 10^{-3}$$

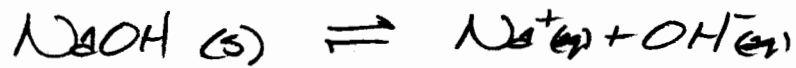
$\therefore$ we need to reduce $[\text{H}^+]$ by adding $[\text{OH}^-]$



could
↓

⑧ could

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

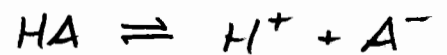


$$\text{MW}_{\text{NaOH}} = 40 \text{ g/mol} \quad \frac{40 \text{ g}}{\text{mol}} \mid \frac{2.7399 \times 10^{-3} \text{ mol}}{\mid} \mid \frac{1000 \text{ mg}}{\text{g}}$$

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

⑨ Look Notes Page 3-22

Governing Equations



$$\textcircled{1} K_w = 10^{-14} = [\text{H}^+][\text{OH}^-]$$

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

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

$$\textcircled{4} [\text{H}^+] = [\text{OH}^-] + [\text{A}^-]$$

4 equations, 4 unknowns:
 $[\text{H}^+]$ $[\text{OH}^-]$ $[\text{HA}]$ $[\text{A}^-]$

Solve For $[\text{H}^+]$

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

From $\textcircled{4}$ $[\text{H}^+] = [\text{A}^-]$

From $\textcircled{2}$ $[\text{HA}] = \frac{[\text{H}^+]^2}{2.47 \times 10^{-7}}$

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

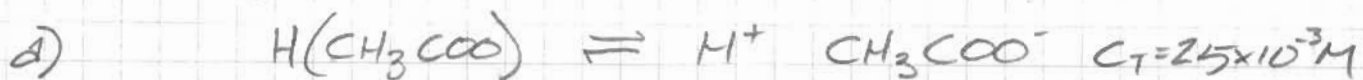
$$\therefore [\text{H}^+] = 9.95 \times 10^{-7} \text{ and } -1.24 \times 10^{-6}$$

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

check
 Assumption

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

⑩ Find pH + concentrations $K_A = 1.8 \times 10^{-5}$



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

$$\textcircled{2} \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{H}(\text{CH}_3\text{COO})]} = 1.8 \times 10^{-5}$$

$$\textcircled{3} [\text{CH}_3\text{COO}^-] + [\text{H}(\text{CH}_3\text{COO})] = 2.5 \times 10^{-3}$$

$$\textcircled{4} [\text{H}^+] = [\text{OH}^-] + [\text{CH}_3\text{COO}^-]$$

Again, Assume $[\text{H}^+] \gg [\text{OH}^-]$
 $\therefore [\text{H}^+] = [\text{CH}_3\text{COO}^-]$

Solve for $[\text{H}^+]$, just like question ⑨

$$[\text{H}^+] = 2.033 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} = 3.69$$

$$[\text{CH}_3\text{COO}^-] = 2.033 \times 10^{-4} \text{ mol/L}$$

$$[\text{OH}^-] = 4.919 \times 10^{-11} \text{ mol/L}$$

$$[\text{H}(\text{CH}_3\text{COO})] = 2.3 \times 10^{-3} \text{ mol/L}$$

$$[\text{H}^+] \gg [\text{OH}^-]$$

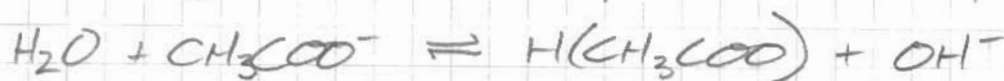
$\therefore$ Assumption
O.K.

b) $2.5 \times 10^{-3} \text{ M Na}(\text{CH}_3\text{COO}^-)$ assume complete dissociation



$$\therefore [\text{Na}(\text{CH}_3\text{COO}^-)] = [\text{Na}^+] = 2.5 \times 10^{-3} \text{ mol/L}$$

but CH_3COO^- will accept H^+ from the water



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

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

$$K_B = \frac{K_w}{K_A} = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

control

⑩ governing equations:

By 3-20
in notes

$$① [H^+][OH^-] = 10^{-14}$$

$$② \frac{[OH^-][H(CH_3COO)]}{[H_2O][CH_3COO^-]} = K_B = 5.56 \times 10^{-10}$$

Electroneutrality
equation

$$③ C_T = [CH_3COO^-] + [H(CH_3COO)] = 2.5 \times 10^{-3}$$

$$④ [Na^+] + [H^+] = [OH^-] + [CH_3COO^-]$$

$$⑤ [Na^+] = 2.5 \times 10^{-3} \text{ mol/L}$$

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

rearrange ④: $[CH_3COO^-] = 2.5 \times 10^{-3} - [OH^-]$

sub into ③: $[H(CH_3COO)] = [OH^-]$

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

$$\therefore [OH^-] = 1.18 \times 10^{-6} \text{ mol/L}$$

$$pH = 8.07$$

$$[H^+] = 8.51 \times 10^{-9} \text{ mol/L}$$

$$[H(CH_3COO)] = 1.18 \times 10^{-6} \text{ mol/L}$$

$$[CH_3COO^-] = 2.5 \times 10^{-3} \text{ mol/L}$$

$$[Na^+] = 2.5 \times 10^{-3} \text{ mol/L}$$

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

$\therefore$ Assump.
O.K.

⑪ a) see Excel sheet

Σ cations $\approx \Sigma$ Anions

$\therefore$ Analysis is reasonable

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

$$\text{Total Hardness} = \left[\frac{[\text{Ca}^{2+}]}{\text{EW}_{\text{Ca}^{2+}}} + \frac{[\text{Mg}^{2+}]}{\text{EW}_{\text{Mg}^{2+}}} + \frac{[\text{Fe}^{2+}]}{\text{EW}_{\text{Fe}^{2+}}} + \frac{[\text{Cd}^{2+}]}{\text{EW}_{\text{Cd}^{2+}}} \right] \times 50 \text{ g CaCO}_3/\text{eq}$$

$$= 821.0 \text{ g/m}^3 \text{ as CaCO}_3 \text{ (water is very hard)}$$

p. 3-8 in notes

NOTE do part d) first

$$\text{d) } [\text{HCO}_3^-] = 260 \text{ g/m}^3 = 4.75 \times 10^{-3} \text{ mol/L}$$

$$\text{pHCO}_3^- = -\log(4.75 \times 10^{-3}) = 2.32$$

$$[\text{CO}_3^{2-}] = 30 \text{ g/m}^3 = 5.0 \times 10^{-4} \text{ mol/L}$$

$$\text{pCO}_3^{2-} = 3.3.$$

looking at Figure 4 From Lab 1 on page 9,
we find $\text{pH} \approx 9.5$

back to c)

$$\begin{aligned} \text{e) Alk} &= [\text{HCO}_3^- + \text{CO}_3^{2-} + \text{OH}^- - \text{H}^+] \times 50 \text{ g CaCO}_3/\text{eq} \\ &= [4.26 \times 10^{-3} + 1 \times 10^{-3} + 3.16 \times 10^{-5} - 3.16 \times 10^{-10}] \\ &= 5.26 \times 10^{-3} \text{ eq/L} \times 50 \text{ g/eq} \times 1000 \text{ L/m}^3 \end{aligned}$$

p. 3-10
in Notes

Note Since $\text{pH} > 8.3$, we use 50 g/eq for CaCO_3

$$\therefore \text{Alk} = 264.5 \text{ g/m}^3 \text{ as CaCO}_3$$

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