



Civil Engineering Department

CVG2132 – FUNDAMENTALS OF ENVIRONMENTAL ENGINEERING

Homework 1 Solutions:
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Due Date: Sept. 26, 2011 (4:00pm) – Cubby « CVG 2132 », Mezzanine A (0.5) CBY

Question 1: (a) A liquid sample has a concentration of Fe (II) of 252.3 mg/L. The density of the liquid is 1543 g/L. What is the Fe concentration in ppm & ppb?

ANS:

- ppm = mg/kg
- ppm = (mg/L) / (kg/L)
- ppm = 252.3 mg/L / 1.543 kg/L
- ppm = 163.5

- ppb = µg /kg
- ppb = (µg /L) / (kg/L)
- ppb = 0.2523 µg/L / 1.543 kg/L
- ppb = 0.1635

(b) Nitrate concentrations exceeding 44.3 mg NO₃⁻/L are a concern in drinking water due to the infant disease, methemoglobinemia. Nitrate concentrations are often recorded in units of NO₃⁻ - N/L to be compared with other nitrogen constituents. Near three rural wells nitrate concentrations were reported as 0.25 mg NO₃⁻ -N/L, 8.7 mg NO₃⁻ -N/L, and 27.3 mg NO₃⁻ -N/L. Do any of these three wells exceed the 44.3 ppm level?

NOTE: NO₃⁻ -N/L is read as nitrate as nitrogen per liter. This example is similar to the methane example that was done together in class, where we express methane concentrations as carbon dioxide as carbon per liter.

ANS:

Convert the regulatory value to units of "as N". Then compare to the measured concentrations.

$$\frac{44.3 \text{ mg } NO_3^-}{L} \times \frac{1 \text{ mole } NO_3^-}{62.0 \text{ g } NO_3^-} \times \frac{1 \text{ mole } N}{1 \text{ mole } NO_3^-} \times \frac{14.0 \text{ g } N}{1 \text{ mole } N} = 10.0 \text{ mg } NO_3^- - N / L$$

The third well (20.0 mg NO₃⁻-N/L) exceeds the 10 ppm level.

Question 2: A water sample contains 10 mg NO₃⁻/L. What is the concentration in a dilute water in units of (a) ppm (b) moles/L, (c) mg NO₃⁻-N/L, and (d) ppb?

ANS:

10 g NO₃⁻/L in various units.

a) 1 L water = 1 kg water (in dilute water solutions: mg/L = ppm)

$$\frac{10 \text{ mg} / \text{L}}{1 \text{ kg} / \text{L}} = \boxed{10 \text{ ppm as NO}_3^-}$$

b) 62 grams NO₃⁻ = 1 mole NO₃⁻

$$\frac{10 \text{ mg}}{\text{L}} \times \frac{1 \text{ g}}{1,000 \text{ mg}} \times \frac{1 \text{ mole}}{62 \text{ g}} = \boxed{1.6 \times 10^{-4} \text{ moles NO}_3^- / \text{L}}$$

c) 62 grams NO₃⁻ = 1 mole NO₃⁻; 14 grams N = 1 mole N; 1 mole NO₃⁻ = 1 mole N

$$\frac{10 \text{ mg NO}_3^-}{\text{L}} \times \frac{1 \text{ mole NO}_3^-}{62 \text{ g NO}_3^-} \times \frac{1 \text{ mole N}}{1 \text{ mole NO}_3^-} \times \frac{14 \text{ g N}}{1 \text{ mole N}} = \boxed{2.3 \text{ mg NO}_3\text{-N/L}}$$

d) 1 L water = 1 kg water; 1 kg = 10⁶ mg; 1 billion = 10⁹ million

$$\frac{10 \text{ mg} / \text{L}}{1 \text{ kg} / \text{L}} \times \frac{1000 \text{ million}}{1 \text{ billion}} = \boxed{10,000 \text{ ppb as NO}_3^-}$$

Question 3: Mirex (MW = 540 g/mol) is a fully chlorinated organic pesticide that was manufactured to control fire ants. Due to its structure, Mirex is very unreactive; thus, it persists in the environment. Lake Erie water samples have had Mirex concentrations measured as high as 0.000007 mg/L and lake trout samples with 0.0000065 mg/g. **(a)** In the water samples, what is the aqueous concentration of Mirex in units of (i) ppb, (ii) ppt, (iii) μM ? **(b)** In the fish samples, what is the concentration of Mirex in fish in (i) ppm, (ii) ppb?

NOTE: Assume the density of Lake Erie water is 1 kg/L.

ANS:

a)

i) $0.000007 \text{ mg/L} \times (1000 \text{ ug} / 1 \text{ mg}) \times (1\text{L} / 1 \text{ kg}) = 0.007 \text{ ug/kg} = 0.007 \text{ ppb}$

ii) $0.000007 \text{ mg/L} \times (1000000 \text{ ng} / 1 \text{ mg}) \times (1\text{L} / 1 \text{ kg}) = 7 \text{ ng/kg} = 7 \text{ ppt}$

iii) $0.000007 \text{ mg/L} \times (1 \text{ mmol} / 540 \text{ mg}) \times (1000 \text{ umol} / \text{mmol}) = 1.3 \times 10^{-5} \text{ uM}$

b)

i) $0.0000065 \text{ mg/g} \times 1000 \text{ g} / \text{kg} = 0.0065 \text{ mg} / \text{kg} = 0.0065 \text{ ppm}$

ii) $0.0000065 \text{ mg/g} \times 1000 \text{ ug} / \text{mg} \times 1000 \text{ g} / \text{kg} = 6.5 \text{ ug} / \text{kg} = 6.5 \text{ ppb}$

Question 4: Determine the equilibrium pH of aqueous solutions of the following strong acids or bases: **(a)** 257 mg/L of HSO_4^- ; **(b)** 10 mM NaOH; **(c)** 75 $\mu\text{g/L}$ of HNO_3 .

ANS:

Because this problem states that these are strong acids and strong bases, we can assume that they will dissociate 100% of their H^+ and OH^- when added to water (we can also see this assumption by observing the magnitude of the pK_a and pK_b for these compounds).

a)

$$257 \text{ mg HSO}_4^- / \text{L} \times (1 \text{ mmol HSO}_4^- / 97 \text{ mg HSO}_4^-) \times (1 \text{ mmol H}^+ / 1 \text{ mmol HSO}_4^-) \times (1 \text{ mol} / 1000 \text{ mmol}) = 2.65 \times 10^{-3} \text{ mol H}^+$$

$$\text{pH} = -\log(2.65 \times 10^{-3}) = 2.6$$

b)

$$\frac{10 \text{ mmole NaOH}}{\text{L}} \times \frac{1 \text{ mole}}{1,000 \text{ mmole}} \times \frac{1 \text{ mole OH}^-}{1 \text{ mole NaOH}} = 0.01 \text{ mole OH}^-$$

$$[\text{OH}^-] = 10^{-2} \quad \text{so} \quad [\text{H}^+] = 10^{-12}$$

$$\boxed{\text{pH} = 12}$$

c)

$$75 \text{ ug HNO}_3 / \text{L} \times (1 \text{ umol HNO}_3 / 63 \text{ ug HNO}_3) \times (1 \text{ umol H}^+ / 1 \text{ umol HNO}_3) \times (1 \text{ mol} / 10^6 \text{ umol}) \\ = 1.19 \times 10^{-6} \text{ mol H}^+$$

$$\text{pH} = -\log(1.19 \times 10^{-6}) = 5.9$$

Question 5: What would be the pH if 7×10^{-3} moles of hydrofluoric acid (HF) were added to 1 L pure water? The $\text{p}K_a$ of HF is 3.2.

ANS:

When HF is added to water, it can either remain as the acid, HF, or dissociate to the base, F^- . Thus, in water we have four unknown species (H^+ , OH^- , HF, F^-). Water is not an unknown because we assume its activity is 1. Thus, in order to solve this problem we require 4 independent equations to solve for the 4 unknowns. The 4 equations are:

$$\text{one mass balance (initial vs. equilibrium): } 7 \times 10^{-3} \text{ moles/L} = [\text{HF}] + [\text{F}^-]$$

$$\text{two equilibrium expressions: } 10^{-14} = [\text{H}^+][\text{OH}^-] \text{ and}$$

$$10^{-3.2} = [\text{H}^+][\text{F}^-]/[\text{HF}]$$

and one expression showing that charge neutrality (**electron balance**) is maintained in the solution

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

The units of the electron balance equation are in N, however due to the fact that "n" for each constituent is one (accept or donate one proton) then $N = M$.

You can solve these expressions simultaneously or make some assumptions to reduce the number of unknowns.

Two assumption methods shown:

Method 1:

Assumption 1: to reduce the mass balance expression, assume $[\text{HF}] > [\text{F}^-]$. This should make sense. We added a lot of a relatively strong acid so we assume that the equilibrium pH is $< \text{p}K_a$. The mass balance then reduces to $[\text{HF}] = 7 \times 10^{-3} \text{ M}$.

Assumption 2: to reduce the electroneutrality expression, assume $[\text{F}^-] > [\text{OH}^-]$. This should also make sense. We added a lot of an acid so the pH should be below 7 where the concentration of OH^- becomes very small. Thus, this expression reduces to $[\text{H}^+] = [\text{F}^-]$.

Substitute these two items into the equilibrium expression for HF.

$$10^{-3.2} = \frac{[H^+][F^-]}{7 \times 10^{-3}} \rightarrow [H^+]^2 = 4.4 \times 10^{-6} \rightarrow [H^+] = 2.1 \times 10^{-3}$$

$$\text{pH} = 2.7$$

Method 2:

Assumption 1: We added a lot of an acid so the pH should be below 7 where the concentration of OH^- becomes very small. Thus, this expression reduces the charge neutrality or “**electron balance**” expression to $[H^+] = [F^-]$.

$$\text{From mass balance equation: } [HF] = 7 \times 10^{-3} \text{ moles/L} - [F^-]$$

$$\text{From assumption 1 (above): } [H^+] = [F^-]$$

$$\text{Plug the above equations into the } K_a \text{ equilibrium equation: } 10^{-3.2} = \frac{[H^+][F^-]}{[HF]}$$
$$\& \text{ therefore } 10^{-3.2} = \frac{[F^-]^2}{(7 \times 10^{-3} \text{ moles/L} - [F^-])}$$

$$\text{Now expand, } [F^-]^2 + 10^{-3.2}[F^-]^2 - 4.4 \times 10^{-6} = 0$$

$$\text{From trial and error or solving: } [F^-] = 10^{-2.6}$$

$$\text{Since } [H^+] = [F^-] \text{ then } [H^+] = 10^{-2.67}$$

$$\text{pH} = 2.7$$

Lastly, we must check our assumptions to make sure they are correct. First we solve for the rest of the unknowns. From the equilibrium expression for HF we can determine that $[F^-] = 2.5 \times 10^{-3}$ and from the equilibrium expression for the dissociation of water, $[\text{OH}^-] = 4 \times 10^{-12}$. Both assumptions are valid, therefore our “approximate” answer is correct.

Question 6: The following properties of a water sample are measured: $\text{pH} = 9.58$, alkalinity from carbonate of 85 mg/L CaCO_3 . What is the quantity of alkalinity (in mg/L CaCO_3) caused by the bicarbonate ion? The alkalinity is only due to inorganic species of C and OH^- .

$$\text{NOTE: Assume } K = 10^{-10.3} = \frac{[H^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

ANS:

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{OH}^-] - [H^+]$$

Because $\text{pH} = 9.58$, assume that you only have CO_3^{2-} , HCO_3^- present in significant quantities

$$\text{pH gives us: } [\text{OH}^-] = 10^{-4.42}; [H^+] = 10^{-9.58} \quad (1)$$

$$K \text{ gives us: } 10^{-10.3} = \frac{[H^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad (2)$$

$$[\text{CO}_3^{2-}] = 85 \text{ mg/L as CaCO}_3 = 0.85 \text{ mM} \quad (3)$$

From (1), (2), (3) we can isolate for $[\text{HCO}_3^-]$

$$[\text{HCO}_3^-] = (10^{-9.58} \text{ M} \cdot 0.00085 \text{ M}) / (10^{-10.3} \text{ M}) = 10^{-2.35} \text{ M} = 272.7 \text{ mg/L as CaCO}_3$$

Question 7: A groundwater is being considered for use as a domestic supply. The water has a temperature of 15°C and the following chemical analysis:

Constituent	Concentration <i>g/m³</i>
Ca ²⁺	145
Mg ²⁺	62
Na ⁺	75
Fe ²⁺	0.7
Cd ²⁺	0.2
HCO ₃ ⁻	285
SO ₄ ²⁻	64
CO ₃ ²⁻	48
Cl ⁻	440
NO ₃ ⁻	35

- What is the hardness of the water in units of mg/L as CaCO₃?
- Determine the alkalinity of the water in units of mg/L as CaCO₃.
- Estimate the sample pH.

NOTE: Assume $K = 10^{-10.3} = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]$

ANS:

(a)

$$[\text{Ca}^{2+}] = 145 \text{ mg Ca}^{2+}/\text{L} \times (1 \text{ mmol Ca}^{2+}/40.1 \text{ mg Ca}^{2+}) \times (1 \text{ mmol CaCO}_3/1 \text{ mmol Ca}^{2+}) \times (100 \text{ mg CaCO}_3/1 \text{ mmol CaCO}_3) = 361.6 \text{ mg CaCO}_3/\text{L}$$

$$[\text{Mg}^{2+}] = 62 \text{ mg Mg}^{2+}/\text{L} \times (1 \text{ mmol Mg}^{2+}/24.8 \text{ mg Mg}^{2+}) \times (1 \text{ mmol CaCO}_3/1 \text{ mmol Mg}^{2+}) \times (100 \text{ mg CaCO}_3/1 \text{ mmol CaCO}_3) = 250 \text{ mg CaCO}_3/\text{L}$$

$$[\text{Fe}^{2+}] = 0.7 \text{ mg Fe}^{2+}/\text{L} \times (1 \text{ mmol Fe}^{2+}/66.9 \text{ mg Fe}^{2+}) \times (1 \text{ mmol CaCO}_3/1 \text{ mmol Fe}^{2+}) \times (100 \text{ mg CaCO}_3/1 \text{ mmol CaCO}_3) = 1.05 \text{ mg CaCO}_3/\text{L}$$

$$[\text{Cd}^{2+}] = 0.2 \text{ mg Cd}^{2+}/\text{L} \times (1 \text{ mmol Cd}^{2+}/112.4 \text{ mg Cd}^{2+}) \times (1 \text{ mmol CaCO}_3/1 \text{ mmol Cd}^{2+}) \times (100 \text{ mg CaCO}_3/1 \text{ mmol CaCO}_3) = 0.18 \text{ mg CaCO}_3/\text{L}$$

$$\text{Total Hardness (TH)} = [\text{Ca}^{2+}] + [\text{Mg}^{2+}] + [\text{Fe}^{2+}] + [\text{Ca}^{2+}]$$

$$\text{TH} = 612.83 \text{ mg CaCO}_3 / \text{L}$$

(b)

$$[\text{CO}_3^{2-}] = 48 \text{ mg CO}_3^{2-}/\text{L} \times (1 \text{ mmol CO}_3^{2-}/60 \text{ CO}_3^{2-}) \times (1 \text{ mmol CaCO}_3/1 \text{ mmol CO}_3^{2-}) \times (100 \text{ mg CaCO}_3/1 \text{ mmol CaCO}_3) = 80 \text{ mg CaCO}_3 / \text{L}$$

$$[\text{HCO}_3^-] = 285 \text{ mg HCO}_3^-/\text{L} \times (1 \text{ mmol HCO}_3^-/61 \text{ HCO}_3^-) \times (1 \text{ mmol CaCO}_3/2 \text{ mmol HCO}_3^-) \times (100 \text{ mg CaCO}_3/1 \text{ mmol CaCO}_3) = 233.6 \text{ mg CaCO}_3 / \text{L}$$

Use K value:

$$K = 10^{-10.3} = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]$$

$$[\text{CO}_3^{2-}] = 48 \text{ mg CO}_3^{2-}/\text{L} \times (1 \text{ g} / 1000 \text{ mg}) \times (1 \text{ mol CO}_3^{2-}/60 \text{ g CO}_3^{2-}) = 0.0008\text{M}$$

$$[\text{HCO}_3^-] = 285 \text{ mg HCO}_3^-/\text{L} \times (1 \text{ g} / 1000 \text{ mg}) \times (1 \text{ mol HCO}_3^-/61 \text{ g HCO}_3^-) = 0.00467\text{M}$$

$$\text{Plug into } K = 10^{-10.3} = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]$$

$$[\text{H}^+] = 2.93 \times 10^{-10}\text{M}$$

$$[\text{OH}^-] = 3.42 \times 10^{-5}\text{M}$$

$$[\text{H}^+] = 2.93 \times 10^{-10} \text{ mol/L} \times (1 \text{ mol CaCO}_3/ 2 \text{ mol H}^+) \times (100 \text{ g CaCO}_3/ 1 \text{ mol CaCO}_3) (1000 \text{ mg} / 1 \text{ g}) = 0.0000147 \text{ mg CaCO}_3 / \text{L}$$

$$[\text{OH}^-] = 3.42 \times 10^{-5} \text{ mol/L} \times (1 \text{ mol CaCO}_3/ 2 \text{ mol OH}^-) \times (100 \text{ g CaCO}_3/ 1 \text{ mol CaCO}_3) (1000 \text{ mg} / 1 \text{ g}) = 1.71 \text{ mg CaCO}_3 / \text{L}$$

$$\text{Alk} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}^+] + [\text{OH}^-]$$

$$\text{Alk} = 315.31 \text{ mg CaCO}_3 / \text{L}$$

(c)

$$\text{pH} = -\log [\text{H}^+]; [\text{H}^+] = 2.93 \times 10^{-10} \text{ mol/L}$$

$$\text{pH} = 9.53$$