Homework #2 - Solutions

Due: April 04, 2018 (Wed), in class

1. You drank three bottles of soju last night. You want to know how much ethanol you drank and how it can be translated into calories. Assume that soju is a pure 17.8%[1] ethanol solution in water (volume ethanol/volume solution) and also that when ethanol is mixed with water, the total volume remains unchanged (for example, 1 L soju contains 178 mL ethanol and 822 mL water). Using the following values, answer the questions.

   density of ethanol = 0.78 kg/L
   density of water = 1.00 kg/L

[1]참이슬 후레쉬 도수

1) Calculate the mass concentration (in g/L), molarity (in M) and mole fraction of ethanol in soju. (10 points)

Answer)

MW of ethanol (C_2H_5OH) = $2 \times 12 + 1 \times 6 + 16 \times 1 = 46\ g/mole$

i) mass concentration

$$0.178\ L\,ethanol/L\,solution \times 0.78\ kg\,ethanol/L\,ethanol \times 10^3\ g/kg = 139\ g/L$$

ii) molarity

$$\frac{139\ g\,ethanol/L\,solution}{46\ g\,ethanol/mole\ ethanol} = 3.02\ M$$

iii) mole fraction

Moles of water in 1 L solution =

$$\frac{(1-0.178)\ L\,water/L\,solution \times 1.00\ kg\,water/L\,water \times 10^3 g/kg}{18\ g/mole} = 45.7\ moles/L$$

$$mole\ fraction(ethanol) = \frac{3.02\ mole/L}{(3.02+45.7)\ mole/L} = 0.0620$$

2) Estimate the mass of ethanol you drank (in grams) and the energy obtained by the intake of ethanol (in kcal). The enthalpy of reaction for combustion of ethanol is -295 kcal/mole. This means that by 1 mole of ethanol you can get 295 kcal of energy (at maximum). A bottle of soju is 360 mL in volume.

(Note: The lethal dose of ethanol is approximately 6 g ethanol/kg body weight. This means for a 60 kg person, 360 g of ethanol can kill. You may get some guide to protect yourselves from drinking soju by the calculation.)

(10 points)

Answer)

i) mass of ethanol

$139\ g/L \times 0.36\ L/bottle \times 3\ bottles = 150\ g$

(One bottle of soju contains 50 g ethanol. Considering the lethal dose of ethanol, to ensure safety, you should not drink more than ~5 bottles in a row!)

ii) Energy obtained

Moles of ethanol intake: $3.02\ mole/L \times 0.36\ L/bottle \times 3\ bottles = 3.26\ moles$

Energy obtained: $3.26\ moles \times 295\ kcal/mole = 962\ kcal$

2. The BOD first-order reaction rate constant for a water sample is determined to be 0.25/d at 20℃. Using the modified van't Hoff-Arrhenius relationship, i) determine the rate constants at 4℃, 14℃ and 24℃ and ii) calculate the time required to degrade 50% of the UBOD in the sample at the three temperatures. The temperature coefficient θ is given as 1.135 for 4-20℃ and 1.056 for 20-30℃.

(15 points)

Answer)

$k_{1_T} = k_{1_{20}} \theta^{T-20}$

4℃: $k_{1_4} = 0.25 \times 1.135^{4-20} = 0.0330/d$

14℃: $k_{1_{14}} = 0.25 \times 1.135^{14-20} = 0.117/d$

24℃: $k_{1_{14}} = 0.25 \times 1.056^{24-20} = 0.311/d$

Time required to degrade 50% UBOD (see the difference!)

$L_t/L_0 = 0.5 = e^{-k_1 t_{1/2}}$

$$t_{1/2} = \frac{\ln 2}{k_1}$$

4℃: $t_{1/2} = \dfrac{\ln 2}{0.0330/d} = 21.0\ days$

14℃: $t_{1/2} = \dfrac{\ln 2}{0.117/d} = 5.92\ days$

24℃: $t_{1/2} = \dfrac{\ln 2}{0.311/d} = 2.23\ days$

3. Using the following data for water sample analysis, answer the followings.

Ions	Concentration (mg/L)
Ca^{2+}	76.0
Mg^{2+}	26.8
Na^{+}	23.0
K^{+}	19.6
Cl^{-}	37.2
SO_4^{2-}	192.0
CO_3^{2-}	2.7
HCO_3^{-}	136.5

1) Determine the acceptance of the analysis. (10 points)

Answer)

Following tables can be constructed for concentration in meq/L:

Cations	*Ion weight*	*Concentration (meq/L)*
Ca^{2+}	*40.1*	*3.79*
Mg^{2+}	*24.3*	*2.21*
Na^{+}	*23.0*	*1.00*
K^{+}	*39.1*	*0.50*
Sum		*7.50*

Ions	*Ion weight*	*Concentration (meq/L)*
Cl^{-}	*35.5*	*1.05*
SO_4^{2-}	*96.1*	*4.00*
CO_3^{2-}	*60.0*	*0.09*
HCO_3^{-}	*61.0*	*2.24*
Sum		*7.38*

$$|\Sigma(anions)-\Sigma(cations)| = |7.38-7.50| = 0.12$$

$$0.1065+0.0155\times\Sigma(anions) = 0.1065+0.0155\times 7.46 = 0.22$$

As the analysis result for the sample satisfies

$|\Sigma(anions)-\Sigma(cations)| \le 0.1065+0.0155\times\Sigma(anions)$, *it is acceptable.*

2) Determine the sodium adsorption ratio (SAR). In terms of the SAR, is the water acceptable for irrigation? (5 points)

Answer)

$$SAR = \frac{(Na^{+})}{\sqrt{\frac{(Ca^{2+})+(Mg^{2+})}{2}}} = \frac{1.00}{\sqrt{\frac{3.79+2.21}{2}}} = 0.577$$

The water is acceptable for irrigation.

3) Estimate the pH of the sample. Use for pK_{a2} value of 10.3 for the dissociation of HCO_3^- into CO_3^{2-} relationship. (6 points)

Answer)

$[HCO_3^-] = 2.24\ mM$

$[CO_3^{2-}] = 0.045\ mM$

$$K_{a2} = 10^{-10.3} = \frac{[H^+][CO_3^2]}{[HCO_3^-]}$$

$$[H^+] = \frac{K_{a2}[HCO_3^-]}{[CO_3^2]} = 10^{-10.3} \times \frac{2.24\ mM}{0.045\ mM} = 2.49 \times 10^{-9}\ M$$

$$pH = -\log[H^+] = -\log(2.49 \times 10^{-9}) = 8.60$$

4) Determine the alkalinity, total hardness and carbonate hardness in mg/L as $CaCO_3$. (9 points)

Answer)

i) Alkalinity

$$Alk = (HCO_3^-) + (CO_2^{2-}) + (OH^-) - (H^+)$$

(OH^-) is obtained as:

$$(OH^-) = \frac{10^{-14}}{2.49 \times 10^{-9}\ M} = 4.01 \times 10^{-6}\ eq/L = 4.01 \times 10^{-3}\ meq/L$$

Thus, (OH^-) is negligible. So is (H^+) of course.

$$Alk = (HCO_3^-) + (CO_2^{2-}) = 2.24 + 0.09 = 2.33\ meq/L$$

In mg/L as $CaCO_3$:

$$2.33\ meq/L \times 50\ mg/meq = 117\ mg/L\ \ as\ \ CaCO_3$$

ii) Total hardness

$$TH = (Ca^{2+}) + (Mg^{2+})$$

Total hardness in mg/L as $CaCO_3$:

$(3.79 + 2.21)\ meq/L \times 50\ mg/meq = 300\ mg/L\ as\ CaCO_3$

iii) Carbonated hardness

As it is found that Alk<TH, CH=Alk.

CH = 117 mg/L as $CaCO_3$

4. 물 속에 존재하는 유기물질을 화학식 $C_{10}H_{19}O_3N$으로 표현할 수 있다고 가정하자. 환경정책기본법 시행령 상 하천의 생활환경기준 중 TOC 기준으로 IV등급을 겨우 만족하는 물은 IV등급의 COD 기준을 만족하겠는가? 다음의 화학식을 이용하시오.

$$C_{10}H_{19}O_3N + 12.5O_2 \rightarrow 9CO_2 + 7H_2O + HCO_3^- + NH_4^+$$

(참조: 법령정보는 http://www.law.go.kr에서 찾아볼 수 있음)

(15 points)

Answer)

$C_{10}H_{19}O_3N$*의 COD/TOC ratio를 구하면,*

$$\frac{12.5 \times 32\ g\ COD}{10 \times 12\ g\ C} = 3.33\ g\ COD/g\ TOC$$

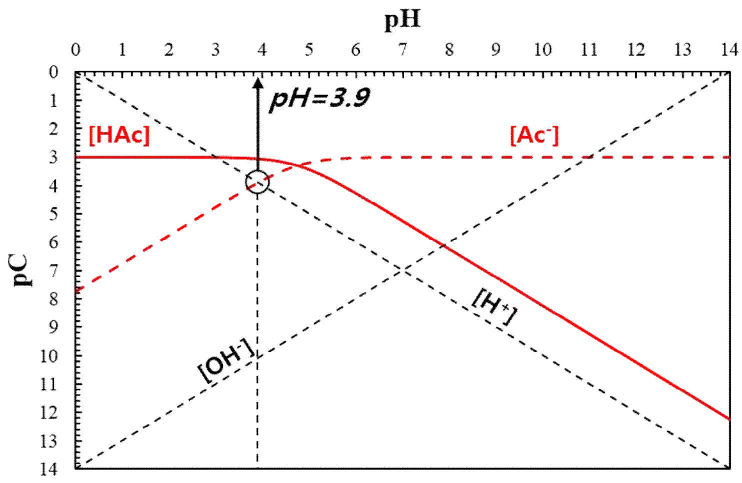
IV등급 하천의 TOC 기준이 6 mg/L 이하이므로, 기준을 겨우 만족하는 물의 COD 값은 20 mg/L임. 따라서 COD 기준인 9 mg/L 이하를 만족하지 않음.

5. 10^{-3} M acetic acid (CH_3COOH; HAc) is dissolved in pure water. For this solution, answer the followings.

1) Draw the pH-pC diagram for 10^{-3} HAc and mark an intersect of the plot that satisfies the charge balance. Estimate the pH of this solution from the intersect. (5 points)

Answer)

The pH-pC diagram is drawn as:



Charge balance: $[H^+] = [Ac^-] + [OH^-]$

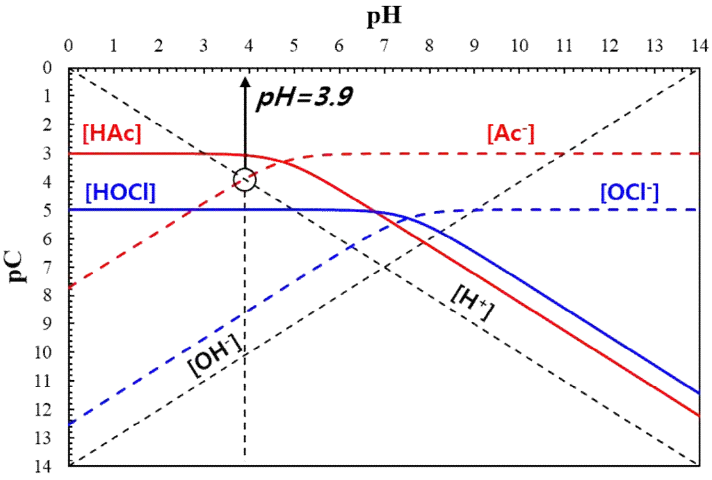
The intersect that satisfies the charge balance is shown above. Note $[H^+] = [Ac^-]$ *and* $[OH^-] \ll [Ac^-]$ *at this point.*

Solution pH = 3.9

2) In the acetic acid solution, 10^{-5} M sodium hypochlorite (NaOCl) is added. On the 10^{-3} HAc pH-pC diagram, plot pC for HOCl and OCl^- at the C_T of 10^{-5} M. Mark the intersection of the pH-pC diagram that satisfies the mass balance and charge balance. Estimate the pH of this solution from the intersect. How does the solution pH change by the addition of NaOCl? (10 points)

Answer)

pH-pC diagram for 10^{-3} *M HAc and* 10^{-5} *M HOCl:*



Mass balances:

$$C_{T,HAc} = 10^{-3}\,M = [HAc] + [Ac^-] \quad (a)$$

$$C_{T,NaOCl} = 10^{-5}\,M = [Na^+] = [HOCl] + [OCl^-] \quad (b)$$

Charge balance:

$$[Na^+] + [H^+] = [OCl^-] + [Ac^-] + [OH^-] \quad (c)$$

From (b) and (c),

$$[HOCl] + [OCl^-] + [H^+] = [OCl^-] + [Ac^-] + [OH^-]$$

$$[HOCl] + [H^+] = [Ac^-] + [OH^-] \quad (d)$$

The intersect that satisfies (d) is shown above. Note $[H^+] = [Ac^-]$, $[OH^-] \ll [Ac^-]$, *and* $[HOCl] \ll [H^+]$ *(pH = 3.9, p[HOCl]=5.0* $\rightarrow$ $[H^+] = 10^{-3.9}$ *M,* $[HOCl] = 10^{-5.0}$ *M) at this point.*

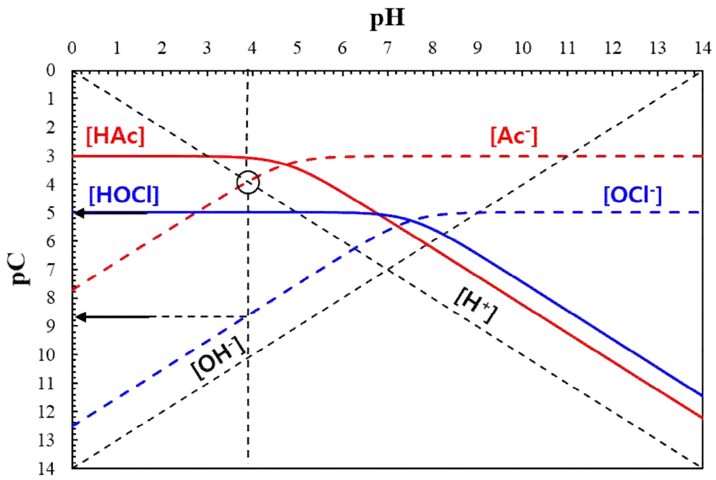
So solution pH=3.9.

The solution pH did not change by the addition of NaOCl. This is because in this system HAc controlled the pH.

3) From the pH-pC diagram, estimate the concentrations of HOCl and OCl^- in the solution.

(5 points)

Answer)



$p[HOCl] = 5.0,\ p[OCl^-] = 8.6$

$[HOCl] = 10^{-5.0}\ M,\ [OCl^-] = 10^{-8.6}\ M$

6. A pH buffer is made using a weak acid and a salt of a conjugate base of the weak acid. For a pH buffer made using a weak monoprotic acid (represented as HA) system, develop a program that can calculate the concentrations of the weak acid (HA; with any pK_a value) and the salt (MA; M represents a well-ionizing metal (i.e., perfectly dissolved in water to be M^+) such as Na and K) that should be added to make a pH buffer solution of any pH and C_T value. You can use any program including Microsoft Excel and MATLAB.

(50 points)