

**Problem Set 6 –Activity and Systematic Approach to Equilibria**

Complete all problems on separate paper. Show all work for credit.

- Write the mass balance expressions for each solution below.
  - 0.100 M in  $\text{H}_3\text{PO}_4$
  - 0.100 M in  $\text{HNO}_2$  and 0.0500 M in  $\text{NaNO}_2$
  - 0.100 M  $\text{Ca}(\text{NO}_3)_2$  saturated with  $\text{CaF}_2$  (s)
- Use the systematic approach to determine the pH of a solution that is 0.100 M in sodium acetate. (Hint: as you go along, determine if you can make any assumptions about the amounts of  $\text{OH}^-$  and  $\text{H}^+$  that are in solution.) (Ignore activity)
- Use the systematic approach to calculate the molar solubility of  $\text{MgCO}_3$  in a solution that has a fixed  $[\text{H}^+] = 1.0 \times 10^{-6}$  M. (Ignore activity)
- Calculate the ionic strength of the following solutions:
  - 0.20 M in  $(\text{NH}_4)_2\text{CrO}_4$
  - 0.10 M in  $\text{CuCl}_2$  and 0.20 M in  $\text{NaCl}$ .
- Find the value of the activity coefficient for  $\text{Cu}^{2+}$  in 0.010 M  $\text{CuCl}_2$  using (a) the extended Debye-Huckel equation and (b) by interpolating the data in a table of activity coefficients. (I promise I won't make you do this very often. ☺)
- Find the pH of a solution that is 0.50 F in benzoic acid and also contains 0.010 M sodium benzoate. (Do not ignore activity.)
- Calculate the solubility of  $\text{FeS}$  in the following situations: (a) pure water, (b) a solution that is also 0.0333 M in  $\text{MgCl}_2$ , (c) a solution that is also 0.020 M in  $\text{K}_2\text{S}$ . (Do not ignore activity, but ignore any subsequent acid-base reactions.)

# Problem Set 6

- ① a)  $0.100M = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]$
- b)  $[HNO_2] + [NO_2^-] = 0.150M$   
 $[H^+] + [HNO_2] = 0.10M$   
 $[Na^+] = 0.0500M$
- c)  $[NO_3^-] = 0.200M$   
 $[Ca^{2+}] = \frac{1}{2}([NO_3^-] + [F^-])$

②  $NaC_2H_3O_2 \rightarrow Na^+ + C_2H_3O_2^-$

$C_2H_3O_2^- + H_2O \rightleftharpoons OH^- + HC_2H_3O_2$        $K_b = 5.7 \times 10^{-10}$

$H_2O \rightleftharpoons H^+ + OH^-$        $K_w = 1 \times 10^{-14}$

CB:  $[Na^+] + [H^+] = [C_2H_3O_2^-] + [OH^-]$

MB:  $[Na^+] = 0.100M$

$[C_2H_3O_2^-]_T = 0.100M = [C_2H_3O_2^-] + [HC_2H_3O_2]$

assume  $[H^+] \ll [Na^+]$  so  $[Na^+] = [C_2H_3O_2^-] + [OH^-] = 0.100M$

then  $[C_2H_3O_2^-] + [OH^-] = [C_2H_3O_2^-] + [HC_2H_3O_2]$

\* or  $[OH^-] = [HC_2H_3O_2]$  ✓

then  $0.100M = [C_2H_3O_2^-] + [HC_2H_3O_2]$

$0.100M = [C_2H_3O_2^-] + [OH^-]$

\* or  $[C_2H_3O_2^-] = 0.100M - [OH^-]$

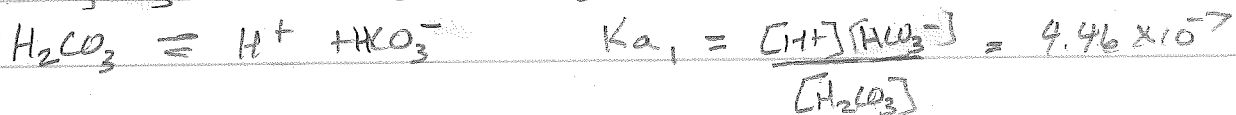
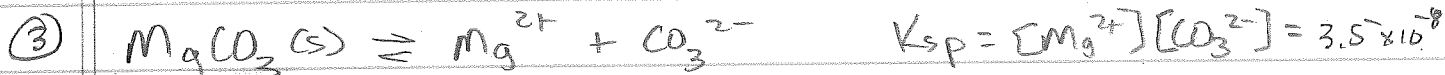
from  $K_b$ :  $K_b = \frac{[OH^-][HC_2H_3O_2]}{[C_2H_3O_2^-]} = \frac{[OH^-][OH^-]}{0.100 - [OH^-]}$

Solving for  $[OH^-]$ :  $[OH^-]^2 + K_b[OH^-] - 0.100K_b = 0$

Use quadratic:  $[OH^-] = 7.55 \times 10^{-6}M, -7.55 \times 10^{-6}M$

$\therefore [H^+] = K_w / 7.55 \times 10^{-6} = 1.33 \times 10^{-9}M$        $pH = \underline{\underline{8.88}}$

notice our assumption is good ( $1.33 \times 10^{-9} \ll 0.100$ )



$$\text{MB! } [\text{Mg}^{2+}] = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]$$

$$\text{From } K_{a2}: [\text{HCO}_3^-] = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_{a2}}$$

$$\text{From } K_{a1}: [\text{H}_2\text{CO}_3] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_{a1}} \Rightarrow [\text{H}_2\text{CO}_3] = \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{K_{a1}K_{a2}}$$

$$\therefore [\text{Mg}^{2+}] = [\text{CO}_3^{2-}] + \frac{[\text{H}^+][\text{CO}_3^{2-}]}{K_{a2}} + \frac{[\text{H}^+]^2[\text{CO}_3^{2-}]}{K_{a1}K_{a2}}$$

$$[\text{Mg}^{2+}] = [\text{CO}_3^{2-}] \left( 1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} \right)$$

$$\text{From } K_{sp}: [\text{CO}_3^{2-}] = \frac{K_{sp}}{[\text{Mg}^{2+}]}$$

$$\text{So } [\text{Mg}^{2+}] = \frac{K_{sp}}{[\text{Mg}^{2+}]} \left( 1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} \right)$$

and

$$[\text{Mg}^{2+}]^2 = K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} \right)$$

$$[\text{Mg}^{2+}] = \sqrt{K_{sp} \left( 1 + \frac{[\text{H}^+]}{K_{a2}} + \frac{[\text{H}^+]^2}{K_{a1}K_{a2}} \right)}$$

$$= 0.049 \text{ M}$$

4 a)  $[NH_4^+] = 0.40M, [CrO_4^{2-}] = 0.20M$

$$\mu = \frac{1}{2}((0.40)(+1)^2 + (0.20)(-2)^2) = 0.60M$$

b)  $[Cu^{2+}] = 0.10M, [Na^+] = 0.20M, [Cl^-] = 0.40M$

$$\mu = \frac{1}{2} [0.10M(+2)^2 + 0.20M(+1)^2 + 0.40M(-1)^2] = 0.50M$$

5.  $[Cu^{2+}] = 0.010M, [Cl^-] = 0.020M$

$$\mu = \frac{1}{2} (0.010M(+2)^2 + 0.020M(-1)^2) = 0.030M$$

a)  $\log \gamma = \frac{-0.51 z^2 \sqrt{\mu}}{1 + \frac{2.5M}{305}} = \frac{-0.51 (+2)^2 \sqrt{0.030}}{1 + \frac{600\sqrt{0.030}}{305}} = 0.264$

$$\gamma = 10^{-0.264} = 0.545$$

b) for  $\mu = 0.01M, \gamma = 0.675$ , for  $\mu = 0.05M, \gamma = 0.485$

$$\frac{0.05 - 0.03}{0.05 - 0.01} = \frac{0.485 - \gamma}{0.485 - 0.675}$$

$$0.5 = \frac{0.485 - \gamma}{-0.19} \Rightarrow \gamma = 0.580$$



I 0.50      0      0.010      \* since we have a buffer solution, we don't expect concentrations to change much (x is small),  $\therefore \mu$  is controlled by sodium benzoate.

C -x      +x      +x

E 0.50-x      x      0.010 +x

$$\mu = \frac{1}{2} (0.010(H)^2 + 0.010(-1)^2) = 0.010M$$

$$\gamma_{H^+} = 0.914, \gamma_{benzoate} = 0.907, \gamma_{benzoic\ acid} = 1$$

$$K_a = \frac{(0.914 [H^+])(0.907 [A^-])}{1 (HA)} = \frac{0.829 (x)(0.010 + x)}{0.50 - x} = 6.28 \times 10^{-5}$$

$$(x)(0.010 - x) = 7.58 \times 10^{-5}$$

$$0.50 - x$$

$$0.010x + x^2 = 3.79 \times 10^{-5} - 7.58 \times 10^{-5} x$$

$$0 = x^2 + 0.01008x - 3.79 \times 10^{-5}$$

$$x = [H^+] = 2.91 \times 10^{-3}$$

$$pH = -\log A_{H^+} = -\log \gamma [H^+] = -\log (0.914 \cdot 2.91 \times 10^{-3}) = 2.57$$

⑦ a) in pure water,  $\mu$  is very small  $\therefore \gamma \approx 1$



$$K_{sp} = 8 \times 10^{-19} = \gamma_{Fe} [Fe^{2+}] \gamma_S [S^{2-}]$$



$$8 \times 10^{-19} = x^2$$



$$x = \boxed{8.9 \times 10^{-10} \text{ M}}$$



$$b) \mu = \frac{1}{2} (0.0333(+2)^2 + 0.0666(-1)^2) = 0.10 \text{ M}$$

$$\gamma_{Fe} = 0.405, \quad \gamma_{S^{2-}} = 0.38$$

$$K_{sp} = (0.405x)(0.38x) = 0.1539x^2$$

$$x = \sqrt{\frac{K_{sp}}{0.1539}} = \boxed{2.28 \times 10^{-9} \text{ M}}$$



Since  $K_{sp}$  is small, expect



$x \ll 0.020 \therefore \mu$  is based



on initial  $[K_2S]$



$$\mu = \frac{1}{2} (0.04 \text{ M}(+1)^2 + 0.02 \text{ M}(-2)^2) = 0.06 \text{ M}$$

Interpolate

$$\frac{0.485 - \gamma_{Fe}}{0.485 - 0.405} = \frac{0.05 - 0.06}{0.05 - 0.10}$$

$$\frac{0.465 - \gamma_S}{0.465 - 0.380} = \frac{0.05 - 0.06}{0.05 - 0.10}$$

$$0.485 - 0.405 \quad 0.05 - 0.10$$

$$0.465 - 0.380 \quad 0.05 - 0.10$$

$$\gamma_{Fe} = 0.469$$

$$\gamma_S = 0.448$$

5

$$K_{sp} = \gamma_{Fe} [Fe^{2+}] \gamma_S [S^{2-}]$$

$$K_{sp} = 0.469 (x) 0.448 (0.020 + x) \quad \text{but } x \ll 0.020$$

$$K_{sp} = 0.469 (x) (0.448) (0.020)$$

$$x = \frac{K_{sp}}{(0.469)(0.448)(0.020)} = \boxed{1.90 \times 10^{-16} \text{ M}}$$

↑  
assumption  
is good!