

HW Assignment Chapter 7

7.4 Finding activity coefficients from table 8-1

- a) $\gamma(\text{SO}_4^{2-} \text{ at } \mu = 0.01) = 0.660$
- b) $\gamma(\text{Sc}^{3+} \text{ at } \mu = 0.005) = 0.54$
- c) $\gamma(\text{Eu}^{3+} \text{ at } \mu = 0.10) = 0.18$
- d) $\gamma[(\text{CH}_3\text{CH}_2)_3\text{NH}^+ \text{ at } \mu = 0.05] = 0.83$

7-9



$$K_{\text{sp}} = [\text{Hg}_2^{2+}] \gamma_{(\text{Hg}_2^{2+})} [\text{Br}^-]^2 \gamma_{(\text{Br}^-)}^2$$

$$2[\text{Hg}_2^{2+}] = [\text{Br}^-]$$

so,

$$K_{\text{sp}} = 4 \gamma_{(\text{Hg}_2^{2+})} \gamma_{(\text{Br}^-)}^2 [\text{Hg}_2^{2+}]^3$$

- a) in 0.00100 M KNO_3
 $[\text{K}^+] = [\text{NO}_3^-] = 0.00100$

$$\mu = \frac{1}{2}[(.001)(+1)^2 + (.001)(-1)^2] = 0.00100$$

$$\gamma(\text{Hg}_2^{2+} \text{ at } \mu = 0.001 \text{ M}) = 0.867$$

$$\gamma(\text{Br}^- \text{ at } \mu = 0.001 \text{ M}) = 0.964$$

$$K_{sp} = 5.6 \cdot 10^{-23} = 4 \gamma_{(\text{Hg}_2^{2+})} \gamma_{(\text{Br}^-)}^2 [\text{Hg}_2^{2+}]^3$$

$$\begin{aligned} [\text{Hg}_2^{2+}] &= (5.6 \cdot 10^{-23}) / [(4) \cdot (0.867) \cdot (0.964)^2] \\ &= 2.6 \cdot 10^{-8} \text{ M} \end{aligned}$$

b) in 0.0100 M KNO_3
 $[\text{K}^+] = [\text{NO}_3^-] = 0.0100$

$$\mu = \frac{1}{2}[(.01)(+1)^2 + (.01)(-1)^2] = 0.0100$$

$$\gamma_{(\text{Hg}_2^{2+})} \text{ at } \mu = 0.01 \text{ M} = 0.660$$

$$\gamma_{(\text{Br}^-)} \text{ at } \mu = 0.01 \text{ M} = 0.901$$

$$K_{sp} = 5.6 \cdot 10^{-23} = 4 \gamma_{(\text{Hg}_2^{2+})} \gamma_{(\text{Br}^-)}^2 [\text{Hg}_2^{2+}]^3$$

$$\begin{aligned} [\text{Hg}_2^{2+}] &= (5.6 \cdot 10^{-23}) / [(4) \cdot (0.660) \cdot (0.901)^2] \\ &= 3.0 \cdot 10^{-8} \text{ M} \end{aligned}$$

c) in 0.100 M KNO_3
 $[\text{K}^+] = [\text{NO}_3^-] = 0.100$

$$\mu = \frac{1}{2}[(.1)(+1)^2 + (.1)(-1)^2] = 0.100$$

$$\gamma_{(\text{Hg}_2^{2+})} \text{ at } \mu = 0.1 \text{ M} = 0.355$$

$$\gamma_{(\text{Br}^-)} \text{ at } \mu = 0.1 \text{ M} = 0.755$$

$$K_{sp} = 5.6 \cdot 10^{-23} = 4 \gamma_{(\text{Hg}_2^{2+})} \gamma_{(\text{Br}^-)}^2 [\text{Hg}_2^{2+}]^3$$

$$\begin{aligned} [\text{Hg}_2^{2+}] &= (5.6 \cdot 10^{-23}) / [(4) \cdot (0.355) \cdot (0.755)^2] \\ &= 4.1 \cdot 10^{-8} \text{ M} \end{aligned}$$

ed 8 in 0.00100 KBr

at first assume an ionic strength of 0.100 from the KBr

$$\mu = \frac{1}{2}[(.001)(+1)^2 + (.001)(-1)^2] = 0.00100$$

$$\gamma(\text{Hg}_2^{2+} \text{ at } \mu = 0.001 \text{ M}) = 0.867$$

$$\gamma(\text{Br}^- \text{ at } \mu = 0.001 \text{ M}) = 0.964$$



$$K_{\text{sp}} = [\text{Hg}_2^{2+}]\gamma_{(\text{Hg}_2^{2+})} [.00100]^2 \gamma_{(\text{Br}^-)}^2$$

$$K_{\text{sp}} = \gamma_{(\text{Hg}_2^{2+})} \gamma_{(\text{Br}^-)}^2 (.00100)^2 [\text{Hg}_2^{2+}]$$

$$\begin{aligned} [\text{Hg}_2^{2+}] &= (5.6\text{e}^{-23}) / [(.000001) * (0.867) * (0.964)^2] \\ &= 6.95\text{E}-17 \text{ M} \end{aligned}$$

Assumption was valid because $[\text{Hg}_2^{2+}]$ is very small.

7-11

$$\mu = \frac{1}{2}\{[\text{H}^+](+1)^2 + [\text{Cl}^-](-1)^2 + [\text{K}^+](+1)^2 + [\text{ClO}_4^-](-1)^2\}$$

$$\mu = \frac{1}{2}\{(.01)(+1)^2 + (.01)(-1)^2 + (.04)(+1)^2 + (.04)(-1)^2\} = 0.0500 \text{ M}$$

$$\gamma(\text{H}^+ \text{ at } \mu = 0.050 \text{ M}) = 0.86$$

$$\begin{aligned} \text{pH} &= -\log [\text{A}(\text{H}^+)] = -\log\{[\text{H}^+](\gamma_{\text{H}^+})\} = -\log[(.01)(.86)] \\ &= 2.07 \end{aligned}$$

7-12

$$\begin{aligned}\mu &= \frac{1}{2}\{[\text{Li}^+](+1)^2 + [\text{NO}_3^-](-1)^2 + [\text{Na}^+](+1)^2 + [\text{OH}^-](-1)^2\} \\ &= \frac{1}{2}\{(0.012)(+1)^2 + (0.012)(-1)^2 + (0.010)(+1)^2 + (0.010)(-1)^2\} \\ &= 0.022 \text{ M}\end{aligned}$$

This lies between 0.01 M ($\gamma(\text{OH}^-) = 0.900$) and 0.05 M ($\gamma(\text{OH}^-) = 0.81$) on Table 8.1. We must extrapolate linearly to obtain $\gamma(\text{OH}^-)$ at $\mu = 0.022$ M.

$$(0.900-x)/(0.900-0.81) = (0.01-0.022)/(0.01-0.05)$$

$$0.900-x = ((-0.012)/(-0.04))*(0.09)$$

$$x = 0.900 - 0.027 = 0.873$$

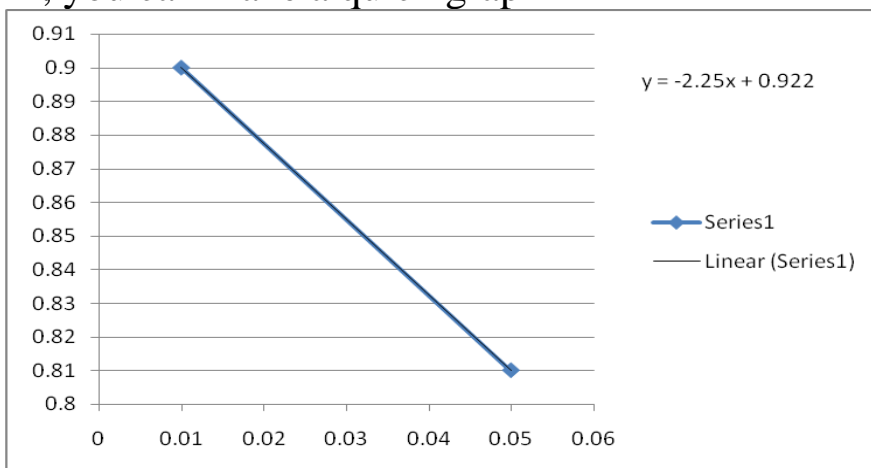
$$\begin{aligned}A_{\text{H}^+} &= [\text{H}^+]\gamma_{\text{H}^+} = K_w/([\text{OH}^-]\gamma_{\text{OH}^-}) = 10^{-14}/[(0.01)*(0.873)] \\ &= 1.2*10^{-12} \text{ M}\end{aligned}$$

$$\text{pH} = -\log A_{\text{H}^+} = 11.94$$

without using activity

$$\text{pH} = \log[\text{H}^+] = 12.00$$

As an alternative to the above method for finding γ_{OH^-} at $\mu = 0.022$ M, you can make a quick graph



7.15

Assume $k = 2$ for benzoic acid

At $m = 0$, $g = 1$ for all species

At $m = .1$, $\gamma(\text{HA}) = 10^{(.2 \cdot .1)} = 1.047$, $\gamma_{\text{A}^-} = 0.80$ and $\gamma(\text{H}^+) = 0.83$

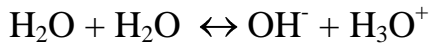
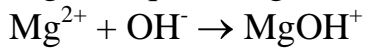
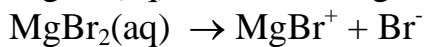
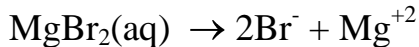
Concentration quotient =

$$\frac{[\text{H}^+][\text{A}^-]/[\text{HA}]}{[\text{H}^+](0.83)[\text{A}^-](0.8)/([\text{HA}]1.047)} =$$

$$1.047/(0.83) \cdot (.80) = 1.58$$

7.21

What are the ions in solution?



Charge balance:

moles of + charges = moles of - charges

each mole of Mg^{2+} carries 2 moles of + charge, each mole of H^+ carries only one + charge, and each mole of OH^- (and Br^-) carries only one mole of negative charge.

$$2[\text{Mg}^{2+}] + [\text{MgBr}^+] + [\text{MgOH}^+] + [\text{H}^+] = [\text{Br}^-] + [\text{OH}^-]$$

Mass balance

2 (total moles Mg) = total moles Br

$$2\{[\text{Mg}^{2+}] + [\text{MgBr}^+] + [\text{MgOH}^+]\} = [\text{MgBr}^+] + [\text{Br}^-] \text{ or}$$

$$2[\text{Mg}^{2+}] + [\text{MgBr}^+] + 2[\text{MgOH}^+] = [\text{Br}^-]$$

b) $0.4 = 2\{[\text{Mg}^{2+}] + [\text{MgBr}^+] + [\text{MgOH}^+]\} = [\text{MgBr}^+] + [\text{Br}^-]$

7.23

$$0.10 \text{ M} = [\text{CH}_3\text{CO}_2^-] + [\text{CH}_3\text{CO}_2\text{H}]$$

7.25

$$3(\text{total mol Fe}) = 2(\text{total mol SO}_4)$$

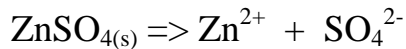
$$3\{\text{Fe}^{3+} + \text{FeOH}_2^+ + \text{Fe}(\text{OH})_2^+ + 2\text{Fe}_2(\text{OH})_2^{4+} + [\text{FeSO}_4^+]\} \\ = 2\{[\text{FeSO}_4^+] + [\text{SO}_4^{2-}] + [\text{HSO}_4^-]\}$$

$$3\text{Fe}^{3+} + 3\text{FeOH}_2^+ + 3\text{Fe}(\text{OH})_2^+ + 6\text{Fe}_2(\text{OH})_2^{4+} + 3[\text{FeSO}_4^+] \\ = 2[\text{FeSO}_4^+] + 2[\text{SO}_4^{2-}] + 2[\text{HSO}_4^-]$$

$$3\text{Fe}^{3+} + 3\text{FeOH}_2^+ + 3\text{Fe}(\text{OH})_2^+ + 6\text{Fe}_2(\text{OH})_2^{4+} + [\text{FeSO}_4^+] \\ = 2[\text{SO}_4^{2-}] + 2[\text{HSO}_4^-]$$

7.28

a



$$\text{Zn}^{2+} + \text{SO}_4^{2-} \Rightarrow \text{ZnSO}_{4(aq)} \quad K_f = \log(2.34) = 0.0045709$$

Mass balance for Zn and SO₄

$$[\text{Zn}^{2+}] + [\text{ZnSO}_{4(aq)}] = 0.01 = [\text{SO}_4^{2-}] + [\text{ZnSO}_{4(aq)}]$$

Simplifying or from charge balance

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

$$K_f = [\text{ZnSO}_{4(aq)}] / [\text{Zn}^{2+}] [\text{SO}_4^{2-}]$$

Let $[\text{Zn}^{2+}] = x$ and make substitutions

$$\log K_f = 2.34$$

$$K_f = 218.78$$

$$K_f = (0.01 - x) / x^2 = 218.78$$

$$X = 0.0004852 \text{ M}$$

b)

$$[\text{Zn}^{2+}] = [\text{SO}_4^{2-}] = 0.004852 \text{ M}$$

$$\mu = \frac{1}{2} (2[(0.00485) \cdot 2^2]) = 0.0194 \text{ M}$$

$$\gamma_{\text{Zn}^{2+}} = 0.630$$

$$\gamma_{\text{SO}_4^{2-}} = 0.609$$

$$K_f = (0.01 - x) / (\gamma_{\text{Zn}^{2+}} \gamma_{\text{SO}_4^{2-}} x^2) = 218.78$$

$$X = 0.006476 \text{ M}$$

Feed this back in to the ionic strength calc

$$[\text{Zn}^{2+}] = [\text{SO}_4^{2-}] = 0.006476 \text{ M}$$

$$\mu = \frac{1}{2} (2[(0.006476) \cdot 2^2]) = 0.0259 \text{ M}$$

$$\gamma_{\text{Zn}^{2+}} = 0.599$$

$$\gamma_{\text{SO}_4^{2-}} = 0.574$$

$$K_f = (0.01 - x) / (\gamma_{\text{Zn}^{2+}} \gamma_{\text{SO}_4^{2-}} x^2) = 218.78$$

$$X = 0.006659 \text{ M}$$

Feed this back in to the ionic strength calc

$$[\text{Zn}^{2+}] = [\text{SO}_4^{2-}] = 0.006659 \text{ M}$$

$$\mu = \frac{1}{2} (2[(0.006659) \cdot 2^2]) = 0.0266 \text{ M}$$

$$\gamma_{\text{Zn}^{2+}} = 0.596$$

$$\gamma_{\text{SO}_4^{2-}} = 0.571$$

$$K_f = (0.01 - x) / (\gamma_{\text{Zn}^{2+}} \gamma_{\text{SO}_4^{2-}} x^2) = 218.78$$

$$X = 0.00668 \text{ M}$$

Feed this back in to the ionic strength calc

$$[\text{Zn}^{2+}] = [\text{SO}_4^{2-}] = 0.00668 \text{ M}$$

$$\mu = \frac{1}{2} (2[(0.00668) \cdot 2^2]) = 0.0267 \text{ M}$$

$$\gamma_{\text{Zn}^{2+}} = 0.596$$

$$\gamma_{\text{SO}_4^{2-}} = 0.570$$

$$K_f = (0.01 - x) / (\gamma_{\text{Zn}^{2+}} \gamma_{\text{SO}_4^{2-}} x^2) = 218.78$$

$$X = 0.006683 \text{ M}$$

ANSWER CONVERGED!!!

$$\% \text{ ion paired} = 100[(0.01 - .00668)/.01] = 33.2 \%$$

