CHEM 201 Self Quiz - 3 (Equilibrium calculations)

1. Write a charge balance for a solution containing H^+, OH^-, Ca^{2+}, HCO_3^-, CO_3^{2-}, $Ca(HCO_3)^+$, $Ca(OH)^+$, K^+, ClO_4^-.

   $[H^+] + 2[Ca^{2+}] + [Ca(HCO_3)^+] + [Ca(OH)^+] + [K^+] =$

   $= [OH^-] + [HCO_3^-] + 2\,[CO_3^{2-}] + [ClO_4^-]$

2. Considering the equilibria below, derive an equation relating $[M^{2+}]$, K_1 and K_2 when 0.10 mol of MX_2 is dissolved in 1 L of water.

$$M^{2+} + X^- \Leftrightarrow MX^+ \qquad K_1 = \frac{[MX^+]}{[M^{2+}][X^-]}$$

$$MX^+ + X^- \Leftrightarrow MX_2(aq) \qquad K_2 = \frac{[MX_{2(aq)}]}{[MX^+][X^-]}$$

$$[MX^+] = K_1[M^{2+}][X^-]$$

$$[MX_{2(aq)}] = K_2[MX^+][X^-] = K_2K_1[M^{2+}][X^-]^2$$

Mass balance equation:

$$MX_2 = \frac{0.10\,mol}{1\,L} = 0.10\,M = [MX_{2(aq)}] + [MX^+] + [M^{2+}] =$$

$$= K_2K_1[M^{2+}][X^-]^2 + K_1[M^{2+}][X^-] + [M^{2+}]$$

Charge balance equation:

$$2\,[M^{2+}] + [MX^+] = [X^-]$$

By substituting of $[M^{2+}]$ and $[MX^-]$ we have an expression for the $[X^-]$

$$2\,[M^{2+}] + K_1[M^{2+}][X^-] = [X^-]$$

By solving this equation for $[X^-]$, we have:

$$[X^-] = \frac{2[M^{2+}]}{1 - K_1[M^{2+}]}$$

Now we put expression for $[X^-]$ into the mass balance equation:

$$0.10\,M = K_2K_1[M^{2+}]\left(\frac{2[M^{2+}]}{1 - K_1[M^{2+}]}\right)^2 + K_1[M^{2+}]\frac{2[M^{2+}]}{1 - K_1[M^{2+}]} + [M^{2+}]$$

3. When ammonium sulfate dissolves, both the anion and cation have acid-base reactions:

$$(NH_4)_2SO_4 \Leftrightarrow 2NH_4^+ + SO_4^{2-} \qquad K_{sp} = 276$$
$$NH_4^+ \Leftrightarrow NH_3(aq) + H^+ \qquad K_a = 5.7 \cdot 10^{-10}$$
$$SO_4^{2-} + H_2O \Leftrightarrow HSO_4^- + OH^- \qquad K_b = 9.8 \cdot 10^{-13}$$

a. write a charge balance for this system

$[NH_4^+] + [H^+] = 2\ [SO_4^{2-}] + [HSO_4^-] + [OH^-]$

b. write a mass balance for this system

$[NH_3] + [NH_4^+] = 2\ \{[SO_4^{2-}] + [HSO_4^-]\}$

c. find the concentration of the $NH_3(aq)$ if the pH is 9.25

$[H^+] = 10^{-9.25}$ and $[OH-] = 10^{-4.75}$

$$\frac{[NH_3][H^+]}{[NH_4^+]} = 5.7 \cdot 10^{-10} = \frac{[NH_3] \cdot 10^{-9.25}}{[NH_4^+]} \quad \Rightarrow \quad \frac{[NH_3]}{[NH_4^+]} = 10^{-0.75} = 1.014$$

Therefore,

$[NH_3] = 1.014\ [NH_4^+]$

From another hand,

$$\frac{[HSO_4^-][OH^-]}{[SO_4^{2-}]} = 9.8 \cdot 10^{-13} = \frac{[HSO_4^-]10^{-4.75}}{[SO_4^{2-}]} \quad \Rightarrow \quad \frac{[HSO_4^-]}{[SO_4^{2-}]} = 9.8 \cdot 10^{-8.25} = 5.51 \cdot 10^{-8}$$

Therefore,

$$[HSO_4^-] = 5.51 \cdot 10^{-8} [SO_4^{2-}]$$

Putting these values of $[NH_3]$ and $[HSO_4^-]$ into the mass balance gives:

$$1.014 \cdot [NH_4^+] + [NH_4^+] = 2\left([SO_4^{2-}] + 5.51 \cdot 10^{-8}[SO_4^{2-}]\right)$$

$$1.007 \cdot [NH_4^+] = [SO_4^{2-}]$$

Now an expression for the K_{sp} is used:

$$K_{sp} = [NH_4^+]^2[SO_4^{2-}] = 1.007\,[NH_4^+]^3 \quad \Rightarrow \quad [NH_4^+] = \sqrt[3]{\frac{276}{1.007}} = 6.5M$$

$$[NH_3] = 1.014[NH_4^+] = 1.014 \cdot 6.5 = 6.59M$$