Midterm Examination March 2, 2017

Due: Beginning of Class, Tuesday, March 7, 2017

Consider a system with three anions, A, B and OH, and three cations, C, D and H. The following reactions are possible

$$AH \overset{K_1}{\longleftrightarrow} A^- + H^+$$
 reaction 1. $BC \overset{K_5}{\longleftrightarrow} B^- + C^+$ reaction 5.

$$AC \stackrel{K_2}{\longleftrightarrow} A^- + C^+$$
 reaction 2. $BD \stackrel{K_6}{\longleftrightarrow} B^- + D^+$ reaction 6.

$$AD \stackrel{K_3}{\longleftrightarrow} A^- + D^+$$
 reaction 3. $COH \stackrel{K_7}{\longleftrightarrow} OH^- + C^+$ reaction 7.

$$BH \stackrel{K_4}{\longleftrightarrow} B^- + H^+$$
 reaction 4. $DOH \stackrel{K_8}{\longleftrightarrow} OH^- + D^+$ reaction 8.

There are a total of fourteen species: AH, AC, AD, BH, BC, BD, COH, DOH, A^{-} , B^{-} , C^{+} , D^{+} , H^{+} , OH^{-} . Equilibrium coefficients govern the distribution of each of these reactions.

$$K_{1} = \frac{\begin{bmatrix} A^{-} \end{bmatrix} H^{+} \\ AH \end{bmatrix}}{\begin{bmatrix} AH \end{bmatrix}} \qquad \text{or} \qquad \begin{bmatrix} AH \end{bmatrix} = \frac{\begin{bmatrix} A^{-} \end{bmatrix} H^{+} \\ K_{1} \end{bmatrix}}{K_{1}} \qquad \text{equation 1.}$$

$$K_{2} = \frac{\begin{bmatrix} A^{-} \end{bmatrix} C^{+} \\ AC \end{bmatrix}}{\begin{bmatrix} AC \end{bmatrix}} \qquad \text{or} \qquad \begin{bmatrix} AC \end{bmatrix} = \frac{\begin{bmatrix} A^{-} \end{bmatrix} C^{+} \\ K_{2} \end{bmatrix}}{K_{2}} \qquad \text{equation 2.}$$

$$K_{3} = \frac{\begin{bmatrix} A^{-} \end{bmatrix} D^{+} \\ AD \end{bmatrix}}{\begin{bmatrix} AD \end{bmatrix}} \qquad \text{or} \qquad \begin{bmatrix} AD \end{bmatrix} = \frac{\begin{bmatrix} A^{-} \end{bmatrix} D^{+} \\ K_{3} \end{bmatrix}}{K_{3}} \qquad \text{equation 3.}$$

$$K_{4} = \frac{\begin{bmatrix} B^{-} \end{bmatrix} H^{+} \\ BH \end{bmatrix}}{\begin{bmatrix} BH \end{bmatrix}} \qquad \text{or} \qquad \begin{bmatrix} BH \end{bmatrix} = \frac{\begin{bmatrix} B^{-} \end{bmatrix} C^{+} \\ K_{4} \end{bmatrix}}{K_{4}} \qquad \text{equation 4.}$$

$$K_{5} = \frac{\begin{bmatrix} B^{-} \end{bmatrix} C^{+} \\ BC \end{bmatrix}}{\begin{bmatrix} BC \end{bmatrix}} \qquad \text{or} \qquad \begin{bmatrix} BC \end{bmatrix} = \frac{\begin{bmatrix} B^{-} \end{bmatrix} D^{+} \\ K_{5} \end{bmatrix}}{K_{5}} \qquad \text{equation 5.}$$

$$K_{6} = \frac{\begin{bmatrix} B^{-} \end{bmatrix} D^{+} \\ BD \end{bmatrix}}{\begin{bmatrix} COH^{-} \end{bmatrix} C^{+} } \qquad \text{or} \qquad \begin{bmatrix} COH^{-} \end{bmatrix} C^{+} \\ K_{7} \qquad \text{equation 7.}$$

Four more equations come from molar balances on A, B, C, D.

 $K_8 = \frac{\left[OH^{-} ID^{+}\right]}{\left[DOH\right]}$

$$[A_{Tot}] = [AH] + [AC] + [AD] + [A^{-}]$$
 equation 9.
$$[B_{Tot}] = [BH] + [BC] + [BD] + [B^{-}]$$
 equation 10.

 $[DOH] = \frac{[OH^{-}]D^{+}}{K}$

equation 8.

$$\begin{bmatrix} C_{Tot} \end{bmatrix} = \begin{bmatrix} AC \end{bmatrix} + \begin{bmatrix} BC \end{bmatrix} + \begin{bmatrix} COH \end{bmatrix} + \begin{bmatrix} C^+ \end{bmatrix}$$
 equation 11.
$$\begin{bmatrix} D_{Tot} \end{bmatrix} = \begin{bmatrix} AD \end{bmatrix} + \begin{bmatrix} BD \end{bmatrix} + \begin{bmatrix} DOH \end{bmatrix} + \begin{bmatrix} D^+ \end{bmatrix}$$
 equation 12.

The pH of the solution is given, which effectively provides the values of both $\left[H^{+}\right]$ and $\left[OH^{-}\right]$.

Solve for the concentration of all fourteen species as a function of pH from 1 to 13 for the following parameter values. Both the equilibrium coefficients and the concentrations have units of $\frac{mol}{\ell}$.

$$\begin{split} K_1 &= 10^{-1}, \ K_2 = 10^{-2}, \ K_3 = 10^{-7}, \ K_4 = 10^{-3}, \ K_5 = 10^{-4}, \ K_6 = 10^{-4}, \ K_7 = 10^{-6} \ \text{and} \ K_8 = 10^{-4}. \\ \left[A_{Tot}\right] &= 1.0 \cdot 10^{-3}, \ \left[B_{Tot}\right] = 0.5 \cdot 10^{-4}, \ \left[C_{Tot}\right] = 1.0 \cdot 10^{-3}, \ \text{and} \ \left[D_{Tot}\right] = 0.5 \cdot 10^{-4}. \end{split}$$