Chemistry 350 | Spring 2018
28 points | Due date Friday, March 9, 2018

Problem Set 4 – Systematic Approach to Equilibria, Buffers

Complete all problems on separate paper. Show all work for credit. Correct use of significant figures is required for full credit. Identify any assumptions you make in solving the problems.

1. An acidic solution containing 0.010 M La^{3+} is treated with NaOH until $La(OH)_3$ precipitates. At what pH does this occur?

$$La(OH)_3 = La^{3+} + 3OH^-$$
$$K_{sp} = [La^{3+}][OH^-]^3$$
$$2 \times 10^{-21} = (0.010\text{ M})[OH^-]^3$$
$$[OH^-] = (2\times10^{-21}/0.010)^{1/3} = 5.85\times10^{-7}\text{M}$$

pOH = 6.23, pH = 7.77

2. In a 0.030 M solution of the weak base, B, 0.27% of B underwent hydrolysis to make BH^+. Find K_b for the base.

If 0.27% undergoes reaction, (0.27/100)*0.030M = 8.1×10^{-5} M BH^+ is produced

	B	+ H_2O	=	OH^-	+	BH^+
I	0.030	-		0		0
C	-8.1×10^{-5}	-		$+8.1\times10^{-5}$		$+8.1\times10^{-5}$
E	0.02992	-		8.1×10^{-5}		8.1×10^{-5}

$$K_b = \frac{[OH^-][BH^+]}{[B]} = \frac{(8.1\times10^{-5})(8.1\times10^{-5})}{0.02992} = \mathbf{2.19\times10^{-7}}$$

3. Write the charge and mass balance expressions for each solution below. Ignore autoprotolysis of water. (4 points each)

   a. 0.100 M in H_3PO_4 : Write the charge balance expression and one mass balance expression.

Charge Balance: $[H^+] = 3[PO_4^{3-}] + 2[HPO_4^{2-}] + [H_2PO_4^-]$
Mass Balance: $0.100\text{ M} = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$

   b. 0.100 M in HNO_2 and 0.0500 M in $NaNO_2$: Write the charge balance expression and two independent mass balance expressions.

Charge Balance: $[H^+] + [Na^+] = [NO_2^-]$
Mass Balance: $0.150\text{ M} = [HNO_2] + [NO_2^-]$
$0.100\text{ M} = [H^+] + [HNO_2]$
$0.050\text{ M} = [Na^+]$

c. 0.100 M $Ca(NO_3)_2$ saturated with CaF_2 (s) : Write the charge balance expression and one mass balance expression.

Charge Balance: $2[Ca^{2+}] = [NO_3^-] + [F^-]$
Mass Balance: $0.200\ M = [NO_3^-]$
$[Ca^{2+}] = ½([NO_3^-] + [F^-])$ (this is same as charge balance)

4. What is the pH of a solution prepared by mixing 20.0 mL of 0.100 M HCl with 150 mL of 0.150 M sodium acetate. Assume volumes are additive. K_a for acetic acid is 1.75 x 10^{-5}.

Here the strong acid HCl will react with the sodium acetate to produce acetic acid, resulting in a buffer solution.

	HCl	+	NaAc	→	NaCl	+	HAc
Start	2.0 mmol		22.5 mmol		0		0
End	0		20.5 mmol		2.0 mmol		2.0 mmol

Now we use H-H equation:

$$pH = pK_a + \log \frac{\text{mol } Ac^-}{\text{mol HAc}} = 4.75 + \log \frac{22.5 \text{ mmol } Ac^-}{2.0 \text{ mmol HAc}} = \mathbf{5.80}$$

5. Describe how you would prepare 0.500 L of 0.100 M imidazole buffer, pH 7.50, starting with imidazole hydrochloride, $pK_a = 6.99$. Assume you also have 1.00 M NaOH and 1.00 M HCl at your disposal. (*hint: 0.100 M refers to the total "imidazole" concentration)*

We need a total of 0.500 L x 0.100 mol/L = 0.050 mol imidazole hydrochloride. This requires:

$$0.050 \text{ mol IHCl} \times \frac{104.54 \text{ g IHCl}}{1 \text{ mol IHCl}} = 5.23 \text{ grams}$$

Since imidazole hydrochloride is a weak acid we know we will need to add some strong base to produce the buffer. We could simple use a pH probe and add NaOH until we reach the target pH. We can also calculate the volume of 1.00 M NaOH needed to do so.

$$pH = pK_{aa} + \log \frac{\text{mol I}}{\text{mol IHCl}} \quad \text{so} \quad 7.50 = 6.99 + \log \frac{\text{mol I}}{\text{mol IHCl}}$$

Rearranging shows us that the ratio of mol I/mol IHCl must be 3.236. Initially, we have 50.0 mmol IHCl, so the total moles of I and IHCl must be 50.0 (because of mass balance). So 50.0 = mol I + mol IHCl

$$3.236 = \frac{\text{mol I}}{\text{mol IHCl}} = \frac{\text{mmol I}}{50 - \text{mmmol I}}$$

Doing some algebra tells us that we need 38.2 mmol I, which wil require adding 38.2 mL of 1.oo M NaOH.