Chemistry 381: Introduction to Biological Chemistry

Homework Assignment # 1

Due: Wed. September 30, 2015 (by 5 pm)

1. How does adding an ionic salt to water lower the freezing point?

2. Calculate the concentration of formate in a 10 mM solution of formic acid at pH 4.15. The pKₐ of formic acid is 3.75.

3. Suppose you have just added 100 mL of a solution containing 0.5 mol of acetic acid per liter to 400 mL of 0.5 M NaOH. What is the final pH? (The pKₐ of acetic acid is 4.7.)

4. Acetic acid has a pKₐ of 4.8. How many milliliters of 0.1 M acetic acid and 0.1 M sodium acetate are required to prepare 1 liter of 0.1 M buffer solution having a pH of 5.8?
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1. How does adding an ionic salt to water lower the freezing point?

Ans.

When ions are dissolved in water it changes the properties. This is because water will accommodate to form bonds with the ions. Water forms hydration shells with these ions making water more structured than it was before. This added structure inhibits the water moving around. This lowers the freezing point because it is more difficult for the water molecules to move into the three-dimensional network that forms to create ice.

2. Calculate the concentration of formate in a 10 mM solution of formic acid at pH 4.15. The pKₐ of formic acid is 3.75.

Ans.

The solution of formic acid contains both the acid species (formic acid) and its conjugate base (formate). Use the H-H equation to determine the ratio of formate (A⁻) to formic acid (HA) at pH 4.15, using the pKₐ value of 3.75.

\[
\text{pH} = \text{pK}_a + \log \left( \frac{[A^-]}{[HA]} \right) \\
\log \left( \frac{[A^-]}{[HA]} \right) = \text{pH} - \text{pK}_a = 4.15 - 3.75 = 0.40 \\
[A^-]/[HA] = 2.51 \text{ or } [A^-] = 2.51[HA]
\]

Since the total concentration of formate and formic acid is 0.01 M, \([A^-] + [HA] = 0.01\) M, and \([HA] = 0.01 - [A^-]\). Therefore,

\[
[A^-] = 2.51 [HA] \\
[A^-] = 2.51 (0.01 M - [A^-]) \\
[A^-] = 0.0251 M - 2.51 [A^-] \\
3.51 [A^-] = 0.0251 M \\
[A^-] = 0.072 M \text{ or } 7.2 \text{ mM}
\]

3. Suppose you have just added 100 mL of a solution containing 0.5 mol of acetic acid per liter to 400 mL of 0.5 M NaOH. What is the final pH? (The pKₐ of acetic acid is 4.7.)

Ans.

Addition of 200 mmol of NaOH (400 mL \(\times\) 0.5 M) to 50 mmol of acetic acid (100 mL \(\times\) 0.5 mM) completely titrates the acid so that it can no longer act as a buffer and leaves 150 mmol of NaOH dissolved in 500 mL, an [OH⁻] of 0.3 M. Given [OH⁻], [H⁺] can be calculated from the water constant:
\[ [\text{H}^+] [\text{OH}^-] = 10^{-14} \]

\[ [\text{H}^+] = 10^{-14} \, \text{M}^2 / 0.3 \, \text{M} \]

pH is, by definition, \( \log(1/[\text{H}^+]) \)

\[ \text{pH} = \log(0.3 \, \text{M} / 10^{-14} \, \text{M}^2) = 13.48. \]

or

\[ (0.5 \, \text{mol/L})(1 \, \text{L} / 1000 \, \text{mL})(100 \, \text{mL}) = 0.05 \, \text{mol acetic acid} \]

\[ (0.5 \, \text{mol/L})(1 \, \text{L} / 1000 \, \text{mL})(400 \, \text{mL}) = 0.2 \, \text{mol NaOH} \]

0.2 mol – 0.05 mol = 0.15 mol OH- remaining after titration

\[ (0.15 \, \text{mol} / 500 \, \text{mL})(1000 \, \text{mL} / \text{1 L}) = 0.3 \, \text{M OH-} \]

\[ \text{pOH} = -\log[\text{OH-}] \]

\[ \text{pOH} = -\log[0.3] \]

\[ \text{pOH} = 0.52 \]

\[ \text{pOH} + \text{pH} = 14 \]

\[ 0.52 + \text{pH} = 14 \]

\[ \text{pH} = 13.48 \]

4. Acetic acid has a pK\(_a\) of 4.8. How many milliliters of 0.1 M acetic acid and 0.1 M sodium acetate are required to prepare 1 liter of 0.1 M buffer solution having a pH of 5.8?

Ans.

Substitute the values of the pK\(_a\) and the desired pH into the Henderson-Hasselbalch equation

\[ 5.8 = 4.8 + \log(\text{acetate}/\text{acetic acid}) \]

Solve for the ratio of acetate to acetic acid.

\[ \log\left(\frac{\text{acetate}}{\text{acetic acid}}\right) = 5.8 - 4.8 = 1.0 \]

\[ \frac{\text{acetate}}{\text{acetic acid}} = 10 \]

For each volume of acetic acid, 10 volumes of acetate must be added (making a total of 11 volumes of the two ionic species). Multiply the proportion of each component by the desired volume.

Acetic acid needed: \( 1/11 \times 1000 \, \text{mL} = 91 \, \text{mL} \)

Acetate needed: \( 10/11 \times 1000 \, \text{mL} = 909 \, \text{mL} \)

Note that when the ratio of the [conjugate base] to [conjugate acid] is 10:1, the pH is exactly one unit above the pK\(_a\). If the ratio were 1:10, the pH would be one unit below the pK\(_a\).