Discussion Exercise 1: Strong acids/bases and monoprotic weak acids

Skill 1: pH of solutions of strong acids and bases

- Strong acids and bases completely ionize, so the concentration of proton and hydroxide can be directly calculated
- $K_W = [H^+][HO^-] = 1 \times 10^{-14}$
- $pH = -log[H^+]$

Problem 1: What is the pH of a 1 mM solution of HCl? What is the pH of a 1×10^{-5} M solution of HCl? What is the pH of a 1×10^{-8} M solution of HCl? (Hint—it is NOT pH 8—you added an acid. What assumption do you make in problems like these?)

Problem 2: What is the pH of a 750 μM solution of NaOH?

Skill 2: Using the Henderson-Hasselbalch equation

- Weak acids and bases do not completely ionize in water; their dissociation equilibrium in water is expressed by $K_A = [A^-][H_3O^+]/[HA]$
- The pK_A value expresses the degree of dissociation; $pK_A = -\log K_A$
- Stronger weak acids have lower pK_A values
- There is a quantitative relationship between the strength of the acid (pKa), the pH of the solution, and the ionization state of the acid (ratio of conjugate base to conjugate acid.) If you know any two of these parameters, you can determine the other. Problems are typically solved by the Henderson-Hasselbalch, which is a rearrangement of the equilibrium expression

$$pH = pKa + log\frac{[A-]}{[HA]}$$

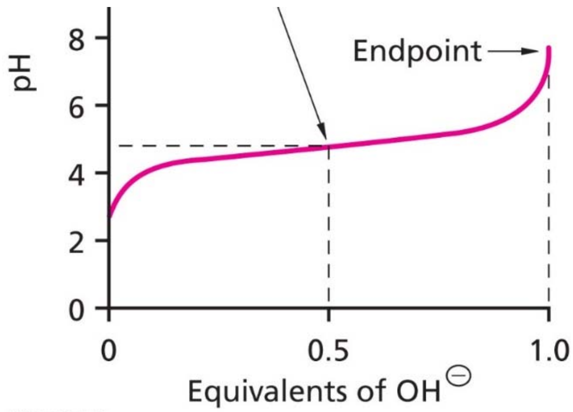
Problem 3: A solution of 2.67g of pyridine was adjusted with HCl until the pyridine was 78% in its protonated (conjugate acid) state. Pyridinium has a pKa of 5.25. What is the pH of the solution?

Problem 4: A common biological buffer is Tris(hydroxymethyl)aminomethane. (Tris for short.) Tris has a pKa of 8.30. What % of Tris molecules are protonated in a solution of pH 7.6?

Skill 3: Graphical analysis using a titration curve

- A weak acid may be titrated by a strong base (and vice versa.)
- When the concentration of conjugate base is close to the concentration of conjugate acid, then the term "log[A-]/[HA]' in the Henderson-Halsselbalch equation is close to zero, and the pH of the solution is close to the pKa of the conjugate acid. When the amount of conjugate acid and conjugate base are exactly equal, then the pH = pKa.
- A titration curve looks like the following graph. This is a titration of acetic acid, with a pKa of 4.7. The endpoint is reached when the amount of base added is equal to the amount of acetic acid present in the solution. This graph is usually given in "equivalents"

rather than absolute concentrations. For example, if a solution of acid contains 80 mmol of the acid, then 1 equivalent is 80 mmol. Adding 40 mmol of hydroxide would be adding 0.5 equivalents. Adding 75 mmol of hydroxide to a solution of 150 mmol of acid would also be adding 0.5 equivalents.



Problem 5. If a solution with 80.0 mmol of acetic acid is treated with 20 mmol of NaOH, then 20 mmol of acetic acid will react to form the conjugate base. How many mmol remain in the conjugate acid form of acetic acid?

Problem 6. Refer to problem 5. Where is this point on the titration graph above? Based on the graph, what is the pH of this solution? Now solve this using the Henderson-Hasselbalch equation. Did you get the same pH value?

Problem 7. Draw a titration curve like the one above for Tris. (See problem 4 for one piece of necessary information.)

Skill 4. Buffers

- Buffers are solutions that resist a change in pH when strong acids or strong bases are added.
- Buffers are able to do this because there is a significant amount of a weak acid present in both its conjugate acid and conjugate base form. These weak acids/bases react with the strong acids/bases to "soak them up" so that they don't change the pH of the solution much.
- Buffers are only effective when they are ± 1.0 pH units away from the pKa of the buffer.

Problem 8. An acetic acid/acetate buffer would only be effective on the range of 3.7 to 5.7. Explain.

Problem 9. What is the ratio of conjugate acid to conjugate base in an acetic acid/acetate buffer at pH 3.7? What is the ratio of conjugate acid to conjugate base in an acetic acid/acetate buffer at pH 5.7? Use the Henderson-Hasselbalch equation to solve for these values.

Problem 10. Draw a titration curve for the acetic acid/acetate buffer, and mark the region in which the buffer is effective.

Problem 11. One liter of a Tris buffer has 100 mmol of tris. If the pH of the solution is 8.0, how many mmol of tris are in the conjugate acid form, and how many are in the conjugate base form?

Problem 12. If the solution from problem 10 is treated with 10 mmol of NaOH, how many mmol of tris are now in the conjugate acid form and the conjugate base form? What is the new pH of the solution?