Experiment 18: A Potentiometric Titration

Background Information

The stoichiometric point is where the moles of OH^- added *equal* the moles of H_3O^{+1} in the sample. It occurs at the steepest point in your graph, as seen in Figure 18.2. This point on the curve is known as the inflection point, which is a calculus term for the point where dy/dx (derivative or slope) is at a maximum, and where $d^2y/dx^2 = 0$ (the 2nd derivative is zero).

Net chemical equation for hydrolysis of a weak acid: $HA + H_2O \rightleftharpoons H_3O^{+1} + A^{-1}$

Equilibrium Constant Expression: $K_a = \frac{[H_3O^{+1}][A^{-1}]}{[HA]}$ and $pK_a = -\log(K_a)$

Where the volume of base is (V/2), at halfway to the stoichiometric point (V), the amount of acid that has been neutralized is half of the total, so $[A^{-1}] = [HA] = 0.5 \times [HA]_0$ at that point. These two values then cancel from K_a, therefore $K_a = [H_3O^{+1}]$ at V/2.
Also at V/2, $pK_a = -\log(K_a) = -\log[H_3O^{+1}] = pH$, where pH is read at V/2 from your graph.

Note that the diprotic acids have two stoichiometric points and two pKa's. pKa_1 equals the pH at (V1)/2, while pKa_2 equals the pH at (V1+V2)/2, midway between the two stoich. pts.

Procedure Notes

- Skip Part A
- Use ~ 0.5 g of solid acid in Step B1.
- Carefully read Laboratory Technique 16c (Titrating a Liquid) in the front of your lab manual for instructions on setting up and using a buret.
- Note that value on buret (volume) increases as the level of titrant liquid decreases. That is, top of buret is 0 ml and bottom is 50 ml.
- pH meter calibration is normally unnecessary, but is accomplished by adjusting the reading to 4.00 with pH 4 buffer using the "standardize" dial, then adjusting the reading to 7.00 with pH 7 buffer using the "slope" dial.
- Add NaOH very slowly (0.2 ml increments) when near stoichiometric point.
- Refer to Figure 18.2 and to Equations 18.2 through 18.8 for your graphs and calculations.
- Note that (moles H_3O^{+1}) = (moles OH^{-1}) at the stoichiometric point.
- **Label and indicate the location of the pKa (V/2) and the stoichiometric point (V) on each of the three graphs.**

Pre-Lab Hints

1. a. CH_3COOH and NaOH reacted together in exact stoichiometric amounts so that both reactants are consumed completely. Only their two products remain in the solution.
   b. NaOH has completely reacted with CH_3COOH, and is no longer present.
   $CH_3COOH_{(aq)}$ has not yet been depleted at the halfway point.
   So, the aqueous acid exists in solution along with the two products (from part a).

2. Refer to paragraph 3 of the background information at the beginning of this handout. Also, refer to Figure 18.2 and to the “pK_a of a Weak Acid” paragraph in the lab manual. Remember that $pK_a = -\log(K_a)$ and $K_a = 10^{-pKa}$.
3. Use (moles H_3O^{+1}) = (moles OH^{-1}) = (moles/L base) × (L base) to find moles of H_3O^{+1}. Then, divide moles of H_3O^{+1} by the acid sample’s volume (convert 25.0 ml to L) to get mol/L for the acid sample. Do **not** add the two volumes together.
4. Make a graph that is similar to Figure 18.2, but **keep the scales <u>linear</u>** for the axes. Label both the **Stoichiometric Point** and the **pKa**.

Line 4	Use V at the stoichiometric point from your graph in 4a.
Line 5	V dispensed equals final (stoichiometric point) minus initial (zero).
Line 7	(moles NaOH) = (moles/L NaOH) × (L NaOH)
Line 8	(moles acid) = (moles NaOH)
Line 9	Molar mass is (g of acid) in Line 1 divided by (moles of H_3O^{+1}) in Line 8.
Line 11	Divide V (line 5) by 2 to get V/2.
Line 12	pK_a = pH at V/2 from your graph in 4a.

5. Skip.

Lab Questions

1. Consider how the moles of acid are determined. How will the calculations for moles and molar mass be affected if 100 ml of DI water, instead of 75 ml, were used to dissolve the solid acid?

2. Suppose the pH meter is miscalibrated so that all readings are 1 point higher than the actual pH. Examine your graphs, and determine how this will affect the volume of NaOH solution (x-axis) at the inflection (stoichiometric) point. Compare your graph with Figure 18.2 to see how pK_a is determined. What will be the overall effect on pKa?

3. The pH reading is initially lower than the equilibrium value immediately after a drop of NaOH solution is added. How do you avoid recording a pH value that is too low? Consider how you found the stoichiometric point on your graph.
   Why is it important to add NaOH slowly and drop-wise near the stoichiometric point? Consider how you would try to find that point if the top part of the curve was incomplete.
   Why is it important to add NaOH until the pH no longer rises dramatically?

4. Suppose NaOH is added too quickly, so that the NaOH volume appears higher at the stoichiometric point. How does this affect the calculated moles of acid?
   How does this affect the acid’s calculated molar mass?
   How does the increased volume affect the determination of pKa?

5. Suppose you chose to analyze a diprotic acid (H_2X). Make a rough sketch of its graph.
   If an acid has more than one H^{+1}, there is a *separate* stoichiometric point for *each* H^{+1}.
   How many stoichiometric points does your sketched graph have?
   How would the NaOH volumes for the points be related mathematically?