CHEM*2400/2480
Summer 2004
Assignment 7

1. How many milliliters of 0.750 M NaOH need to be added to a solution formed by dissolving 4.47 g of malonic acid (MW = 104.062 g/mol; $pK_{a1} = 2.847$; $pK_{a2} = 5.696$) in 500.0 mL of water, if the desired final pH is 5.15?

2. Leucine is an amino acid ($K_{a1} = 4.69 \times 10^{-3}$; $K_{a2} = 1.79 \times 10^{-10}$) which can be obtained in three different forms. If 1.00 g of each is weighed out and dissolved separately in 100.0 mL of water, what is the pH of each resulting solution? The three compounds are: Leucine-hydrochloride, Leucine (MW = 131.173 g/mol), and Sodium Leucinate.

3. Glutamic acid is a triprotic amino acid ($K_{a1} = 5.91 \times 10^{-3}$; $K_{a2} = 3.78 \times 10^{-5}$; $K_{a3} = 1.12 \times 10^{-10}$). The human body buffers its blood at a pH of 7.400. If free glutamic acid is found at a concentration of 0.100 mM, what is the concentration of each form?

4. In dealing with the intermediate form of a polyprotic acid, we used an approximation of setting the formal concentration to be taken to be that of the intermediate forms actual concentration and this lead to a quick solution of the problem. Consider three hypothetical diprotic acids: (a) $K_{a1} = 1.00 \times 10^{-2}$ and $K_{a2} = 1.00 \times 10^{-3}$, (b ) $K_{a1} = 1.00 \times 10^{-5}$ and $K_{a2} = 1.00 \times 10^{-6}$, and (c ) $K_{a1} = 1.00 \times 10^{-5}$ and $K_{a2} = 1.00 \times 10^{-8}$. In each case, the intermediate form is added to sufficient water to produce of 0.0100 F solution of each acid. Use an iterative solution to find the exact pH and concentration of each species and compare the result in each case with the approximation that we would normally use.

5. Consider the titration of 50.00 mL of 0.0250 M phthalic acid ($pK_{a1} = 2.950$; $pK_{a2} = 5.408$) with 0.0500 M NaOH. Calculate the pH at intervals of 5.00 mL from 0.00 mL of added titrant through to 60.00 mL of added titrant. Sketch the titration curve that results. (Note: Don't use the complete equations found at the end of Chapter 12; that is for the next question. Use the approximate equations as appropriate at each point. This is the kind of problem I can ask you to do on the final because you obviously won't have a computer that is needed for using the complete solution.)

6. Use the complete titration equations and a spreadsheet to calculate the titration curve (go out at least 10.00 mL beyond the final endpoint) for the following situations:
   (a) Titration of 50.00 mL of 0.0100 F methylamine ($K_a = 2.31 \times 10^{-11}$) with 0.0125 M HCl.
   (b) Titration of 50.00 mL of 0.0100 F oxalic acid ($K_{a1} = 5.60 \times 10^{-2}$; $K_{a2} = 5.42 \times 10^{-5}$) with 0.0125 M NaOH.
   (c) Titration of 50.00 mL of 0.0100 F lysine-HCl (the fully protonated form of the amino acid: $K_{a1} = 9.14 \times 10^{-3}$; $K_{a2} = 8.29 \times 10^{-10}$; $K_{a3} = 2.00 \times 10^{-11}$) with 0.0125 M NaOH.

   Choose the starting pH carefully so that your first data point has an added volume of <1 mL. Then choose the final pH so that it is beyond the endpoint, but not too far so as to scrunch the whole titration curve up on your plot. If you go too far, the volume becomes negative; watch out for that.

7. In the accompanying table, there is a data set of a titration of a monoprotic acid. (a) Calculate second derivatives to find the equivalence point. (b) Find the equivalence point with a Gran plot. Try to report the endpoint to a precision of 0.01 mL.

| Volume of added (base) | pH |
|---|---|
| 0 | 3.18 |
| 5 | 3.71 |
| 10 | 4.02 |
| 15 | 4.29 |
| 20 | 4.53 |
| 25 | 4.75 |
| 30 | 5.08 |
| 35 | 5.63 |
| 36 | 5.88 |
| 37 | 6.53 |
| 38 | 10.02 |
| 39 | 10.37 |
| 40 | 10.58 |
| 45 | 11.02 |
| 50 | 11.22 |