

CHEM*2400/2480
Summer 2004
Assignment 7

ANSWERS

1. This is a buffer question. We simply need to find the ratio of the base-to-acid concentrations and use the Henderson-Hasselbalch equation. What makes this problem a little more interesting is that it is a diprotic acid. While using the equation for either proton 1 or 2 would work, the data will be easily obtainable for only one instance. A buffer is most useful when it is within ± 1 pH unit of the pK_a value. Since the target pH is 5.15, we will use the pK_a which is closest to that value, in this case, pK_{a2} . We first need to know the amount of H_2M added.

$$n(H_2M) = \frac{4.47 \text{ g}}{104.062 \frac{\text{g}}{\text{mol}}} = 0.0430 \text{ mol}$$

We could determine the formal concentration from this, but we are really only interested in the concentration ratio which is identical to the mole ratio, since they are both in the same volume. So we won't go that unnecessary step.

The required ratio comes from the Henderson-Hasselbalch equation.

$$pH = pK_{a2} + \log \frac{n(M^{2-})}{n(HM^-)}$$

$$5.150 = 5.696 + \log \frac{n(M^{2-})}{n(HM^-)}$$

$$\log \frac{n(M^{2-})}{n(HM^-)} = 5.150 - 5.696 = -0.546$$

$$\frac{n(M^{2-})}{n(HM^-)} = 10^{-0.546} = 0.284$$

We start with H_2M and add base until we convert it all to HM^- : this requires 0.0430 mol of NaOH. We then add a little more base to convert some of the HM^- to M^{2-} , sufficient to achieve the ratio calculated above.

$$n(M^{2-}) = 0.284 n(HM^-) \quad n(HM^-) = 0.0430 - n(M^{2-})$$

$$\therefore n(M^{2-}) = 0.284(0.0430 - n(M^{2-})) = 0.0122 - 0.284 n(M^{2-})$$

$$1.284 n(M^{2-}) = 0.0122 \quad n(M^{2-}) = \frac{0.0122}{1.284} = 0.00951 \text{ mol}$$

This is the amount of base needed beyond the conversion of H_2M to HM^- . The total amount of added base must therefore be

$$n(OH^-) = 0.0430 + 0.00951 = 0.0525 \text{ mol}$$

But we want to know the volume of NaOH solution to add.

$$V(OH^-) = \frac{0.0525 \text{ mol}}{0.750 \text{ M}} = 0.0700 \text{ L} = 70.0 \text{ mL}$$

2. The molar mass of each compound is different because of the counter ions. In the case of the leucine-hydrochloride, an HCl is added to the leucine. In the case of the sodium leucinate, a proton is removed and replaced by a Na ion. The molar masses are then given by:

$$\begin{aligned} \text{MM(L-HCl)} &= 167.634 \text{ g/mol} \\ \text{MM(L)} &= 131.173 \text{ g/mol} \\ \text{MM(NaL)} &= 153.155 \text{ g/mol} \end{aligned}$$

Since the weighed mass is the same in each case, the number of moles employed must be different. We find

$$n(\text{L-HCl}) = \frac{1.00 \text{ g}}{167.634 \frac{\text{g}}{\text{mol}}} = 0.00596 \text{ mol}$$

$$n(\text{L}) = \frac{1.00 \text{ g}}{131.173 \frac{\text{g}}{\text{mol}}} = 0.00762 \text{ mol}$$

$$n(\text{NaL}) = \frac{1.00 \text{ g}}{153.155 \frac{\text{g}}{\text{mol}}} = 0.00653 \text{ mol}$$

The leucine hydrochloride introduces the fully acidic form of the molecule into solution. The sodium leucinate delivers the fully basic form. Leucine itself is the intermediate form. In the case of L-HCl and NaL, we use the quadratic solution for the pH while we need to use the intermediate form equation in the case of the leucine.

(a) leucine hydrochloride:

$$F(\text{L-HCl}) = \frac{0.00596 \text{ mol}}{0.1000 \text{ L}} = 0.0596 \text{ M}$$

$$[\text{H}^+] = \frac{-K_{a1} + \sqrt{K_{a1}^2 + 4K_{a1}F}}{2} = 0.0145 \text{ M}$$

$$\text{pH} = 1.838$$

(b) leucine:

$$F(\text{L}) = \frac{0.00762 \text{ mol}}{0.1000 \text{ L}} = 0.0762 \text{ M}$$

$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} = 8.90 \times 10^{-7} \text{ M}$$

$$\text{pH} = 6.051$$

$$\text{alternate method as check: } \text{pH} = \frac{1}{2}(pK_{a1} + pK_{a2}) = 6.038$$

(c) sodium leucinate:

$$F(\text{NaL}) = \frac{0.00653 \text{ mol}}{0.1000 \text{ L}} = 0.0653 \text{ M}$$

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.01 \times 10^{-14}}{1.79 \times 10^{-10}} = 5.64 \times 10^{-5}$$

$$[\text{OH}^-] = \frac{-K_{b1} + \sqrt{K_{b1}^2 + 4K_{b1}F}}{2} = 0.00189 \text{ M}$$

$$\text{pOH} = 2.723$$

$$\text{pH} = 14 - \text{pOH} = 14 - 2.723 = 11.277$$

3. This is just a direct application of the fractional composition equations. We need only find the $[\text{H}^+]$ and then work out the value for each species. Remember that

these are fractional compositions, so that the results are not in terms of concentrations but rather are numbers that range from 0 to 1.

$$pH = 7.400 \quad [H^+] = 10^{-pH} = 10^{-7.400} = 3.98 \times 10^{-8} \text{ M}$$

$$\alpha_{H_3A} = \frac{[H^+]^3}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} = 7.06 \times 10^{-9}$$

$$\alpha_{H_2A^-} = \frac{K_{a1}[H^+]^2}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} = 1.05 \times 10^{-3}$$

$$\alpha_{HA^{2-}} = \frac{K_{a1}K_{a2}[H^+]}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} = 0.996$$

$$\alpha_{A^{3-}} = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3 + K_{a1}[H^+]^2 + K_{a1}K_{a2}[H^+] + K_{a1}K_{a2}K_{a3}} = 2.80 \times 10^{-3}$$

Concentration is found by multiplying the formal concentration by each fractional composition. We have

$$[H_3A] = 7.06 \times 10^{-9} (0.100 \text{ mM}) = 7.06 \times 10^{-10} \text{ mM} = 7.06 \times 10^{-13} \text{ M}$$

$$[H_2A^-] = 1.05 \times 10^{-3} (0.100 \text{ mM}) = 1.05 \times 10^{-4} \text{ mM} = 1.05 \times 10^{-7} \text{ M}$$

$$[HA^{2-}] = 0.996 (0.100 \text{ mM}) = 9.96 \times 10^{-2} \text{ mM} = 9.96 \times 10^{-5} \text{ M}$$

$$[A^{3-}] = 2.08 \times 10^{-3} (0.100 \text{ mM}) = 2.08 \times 10^{-4} \text{ mM} = 2.08 \times 10^{-7} \text{ M}$$

4. The iterative procedure proceeds as follows:

- (a) Use the formal concentration as $[HM^-]$ in the intermediate equation to calculate a value for $[H^+]$.
- (b) Use these two values for $[HM^-]$ and $[H^+]$ in the two equilibrium expressions (K_{a1} and K_{a2}) to find values for $[H_2M]$ and $[A^{2-}]$.
- (c) Find a new approximation for $[HM^-]_{i+1} = F - [H_2M]_i - [A^{2-}]_i$.
- (d) Rinse and repeat (iterate through steps b and c) until $[HM^-]$ is sufficiently stable, meaning $|[HM^-]_i - [HM^-]_{i-1}|/[HM^-]_i < 0.001$?

The approximation is simply the value for $[H^+]$ found in the first pass of this routine.

- (i) Approximate pH = 2.651
Exact Results (about 25 iterations):
 $[H^+] = 1.92 \text{ mM}$ pH = 2.717
 $[H_2M] = 1.12 \text{ mM}$
 $[HM^-] = 5.84 \text{ mM}$
 $[M^{2-}] = 3.04 \text{ mM}$

- (ii) Approximate pH = 5.500₂
Exact Results (about 10 iterations):
 $[H^+] = 3.16 \times 10^{-6} \text{ M}$ pH = 5.500₄
 $[H_2M] = 1.94 \times 10^{-3} \text{ M}$
 $[HM^-] = 6.13 \times 10^{-3} \text{ M}$
 $[M^{2-}] = 1.94 \times 10^{-3} \text{ M}$

- (iii) Approximate pH = 6.500₂
Exact Results (about 5 iterations):
 $[H^+] = 3.16 \times 10^{-7} \text{ M}$ pH = 6.500₂

$$[\text{H}_2\text{M}] = 2.97 \times 10^{-4} \text{ M}$$

$$[\text{HM}^-] = 9.41 \times 10^{-3} \text{ M}$$

$$[\text{M}^{2-}] = 2.98 \times 10^{-4} \text{ M}$$

You will note how the error was only 0.05 pH unit in the worst case, where the pK_a difference was only a factor of 10 and the pH was very low. In the other cases, the approximate result was accurate to a precision greater than the input data would justify. This clearly confirms the validity of the approximation method in almost all circumstances. However, it should also be noted that the assumption that there is insignificant amount of dissociation is not true and even in the best case, the amount of dissociation is still about 6%; but this turns out to not have a big effect on the pH.

5. Here is the procedure for calculating points on a titration curve, involving a diprotic acid.
 - Use the quadratic equation with K_{a1} for the starting pH.
 - Use the quadratic equation with K_{b1} for the second equivalence point pH.
 - Use the intermediate equation for the first equivalence point pH.
 - Use the Henderson-Hasselbalch equation for all points between the equivalence points (K_{a1} for the first buffer region and K_{a2} for the second).
 - Just consider dilution of the titrant beyond the last equivalence point.

Remember throughout to adjust any formal concentration for dilution effects to that point in the titration. Also, throughout the buffer regions, you only need the ratio of the concentrations which is identical to the mole ratio; using moles rather than concentrations always eliminates some unnecessary calculation steps and nicely accounts for dilution effects at the same time.

From the initial concentrations and volumes, it is easy to see that, since the titrant has twice the concentration of the analyte, that the first equivalence point will be found at a volume equal to half the original analyte volume, namely 25.00 mL.

The second equivalence point is then necessarily at 50.00 mL of added titrant.

Taking the titration to 60.00 mL goes out 10.00 mL beyond the last equivalence point.

$$V = 0.00 \text{ mL} \quad n(\text{H}_2\text{M}) = 0.0250 \text{ M} \times 0.05000 \text{ L} = 1.25 \times 10^{-3} \text{ mol}$$

$$[\text{H}^+] = \frac{-K_{a1} + \sqrt{K_{a1}^2 + 4K_{a1}F}}{2} = 4.76 \times 10^{-3} \text{ M} \quad \text{pH} = 2.322$$

$$V = 5.00 \text{ mL} \quad n(\text{OH}^-) = 0.0500 \text{ M} \times 0.0500 \text{ L} = 2.50 \times 10^{-4} \text{ mol}$$

$$n(\text{HM}^-) = n(\text{OH}^-) = 2.50 \times 10^{-4} \text{ mol}$$

$$n(\text{H}_2\text{M}) = 1.25 \times 10^{-3} - 2.50 \times 10^{-4} = 1.00 \times 10^{-3} \text{ mol}$$

$$\text{pH} = \text{pK}_{a1} + \log \frac{[\text{HM}^-]}{[\text{H}_2\text{M}]} = 2.950 + \log \frac{2.50 \times 10^{-4}}{1.00 \times 10^{-3}} = 2.348$$

The pattern continues through the first buffer region:

$$V = 10.00 \text{ mL} \quad n(\text{OH}^-) = 0.0500 \text{ M} \times 0.01000 \text{ L} = 5.00 \times 10^{-4} \text{ mol}$$

$$n(\text{HM}^-) = n(\text{OH}^-) = 5.00 \times 10^{-4} \text{ mol}$$

$$n(\text{H}_2\text{M}) = 1.25 \times 10^{-3} - 5.00 \times 10^{-4} = 7.50 \times 10^{-4} \text{ mol}$$

$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{HM}^-]}{[\text{H}_2\text{M}]} = 2.950 + \log \frac{5.00 \times 10^{-4}}{7.50 \times 10^{-4}} = 2.774$$

And so on...

$$V = 15.00 \text{ mL} \quad n(\text{OH}^-) = 0.0500 \text{ M} \times 0.01500 \text{ L} = 7.50 \times 10^{-4} \text{ mol}$$

$$n(\text{HM}^-) = n(\text{OH}^-) = 7.50 \times 10^{-4} \text{ mol}$$

$$n(\text{H}_2\text{M}) = 1.25 \times 10^{-3} - 7.50 \times 10^{-4} = 5.00 \times 10^{-4} \text{ mol}$$

$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{HM}^-]}{[\text{H}_2\text{M}]} = 2.950 + \log \frac{7.50 \times 10^{-4}}{5.00 \times 10^{-4}} = 3.126$$

and again...

$$V = 20.00 \text{ mL} \quad n(\text{OH}^-) = 0.0500 \text{ M} \times 0.02000 \text{ L} = 1.00 \times 10^{-3} \text{ mol}$$

$$n(\text{HM}^-) = n(\text{OH}^-) = 1.00 \times 10^{-3} \text{ mol}$$

$$n(\text{H}_2\text{M}) = 1.25 \times 10^{-3} - 1.00 \times 10^{-3} = 2.50 \times 10^{-4} \text{ mol}$$

$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{HM}^-]}{[\text{H}_2\text{M}]} = 2.950 + \log \frac{1.00 \times 10^{-3}}{2.50 \times 10^{-4}} = 3.552$$

Another data point that we did not hit, but is easy to calculate is the 1/2 E.P., where the $\text{pH} = \text{p}K_a$. Hence at

$$V = 12.50 \text{ mL} \quad \text{pH} = \text{p}K_{a1} = 2.950$$

The next point is the first equivalence point where we use the intermediate form equation to find the pH.

$$V = 25.00 \text{ mL} \quad F = 0.0250 \text{ M} \times \frac{50.00}{50.00 + 25.00} = 0.01667 \text{ M}$$

$$[\text{H}^+] = \sqrt{\frac{K_{a1}K_{a2}F + K_{a1}K_w}{K_{a1} + F}} = 6.40 \times 10^{-5} \text{ M} \quad \text{pH} = 4.194$$

Now we move into the second buffer region. We need to find the ratio of HM^- and M^{2-} and we use $\text{p}K_{a2}$ in the buffer equation.

$$V = 30.00 \text{ mL} \quad n(\text{OH}^-)_{\text{beyond 1st E.P.}} = 0.0500 \text{ M} \times 0.00500 \text{ L} = 2.50 \times 10^{-4} \text{ mol}$$

$$n(\text{M}^{2-})_{\text{beyond 1st E.P.}} = n(\text{OH}^-)_{\text{beyond 1st E.P.}} = 2.50 \times 10^{-4} \text{ mol}$$

$$n(\text{HM}^-) = 1.25 \times 10^{-3} - 2.50 \times 10^{-4} = 1.00 \times 10^{-3} \text{ mol}$$

$$\text{pH} = \text{p}K_{a2} + \log \frac{[\text{M}^{2-}]}{[\text{HM}^-]} = 5.408 + \log \frac{2.50 \times 10^{-4}}{1.00 \times 10^{-3}} = 4.806$$

And without belabouring the point, the next three values are

$$V = 35.00 \text{ mL} \quad \text{pH} = 5.232$$

$$V = 40.00 \text{ mL} \quad \text{pH} = 5.584$$

$$V = 45.00 \text{ mL} \quad \text{pH} = 6.010$$

Also, the pH at the 1/2 E.P. point is easily given again.

$$V = 25.00 + 12.50 = 37.50 \text{ mL} \quad \text{pH} = \text{p}K_{a2} = 5.408$$

Now we are at the second equivalence point. We first need to turn K_{a2} into K_{b1} and then use the quadratic solution for $[\text{OH}^-]$ which in turn will give the pH.

$$V = 50.00 \text{ mL} \quad F = 0.0250 \text{ M} \times \frac{50.00}{50.00 + 50.00} = 0.0125 \text{ M}$$

$$K_{b1} = \frac{K_w}{K_{a2}} = \frac{1.01 \times 10^{-14}}{3.90 \times 10^{-6}} = 2.59 \times 10^{-9}$$

$$[\text{H}^+] = \frac{-K_{b1} + \sqrt{K_{b1}^2 + 4K_{b1}F}}{2} = 5.69 \times 10^{-6} \text{ M}$$

$$\text{pOH} = 5.245 \quad \text{pH} = 14 - \text{pOH} = 14 - 5.245 = 8.755$$

The last two points only need to account for dilution of the excess added strong titrant. Remember that you will be directly calculating the pOH which then needs to be turned into the pH.

$$V = 55.00 \text{ mL}$$

$$[\text{OH}^-] = 0.0500 \text{ M} \times \left(\frac{5.00}{50.00 + 55.00} \right) = 2.38 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.623 \quad \text{pH} = 14 - 2.623 = 11.377$$

$$V = 60.00 \text{ mL}$$

$$[\text{OH}^-] = 0.0500 \text{ M} \times \left(\frac{10.00}{50.00 + 60.00} \right) = 4.545 \times 10^{-3} \text{ M}$$

$$\text{pOH} = 2.342 \quad \text{pH} = 14 - 2.342 = 11.658$$

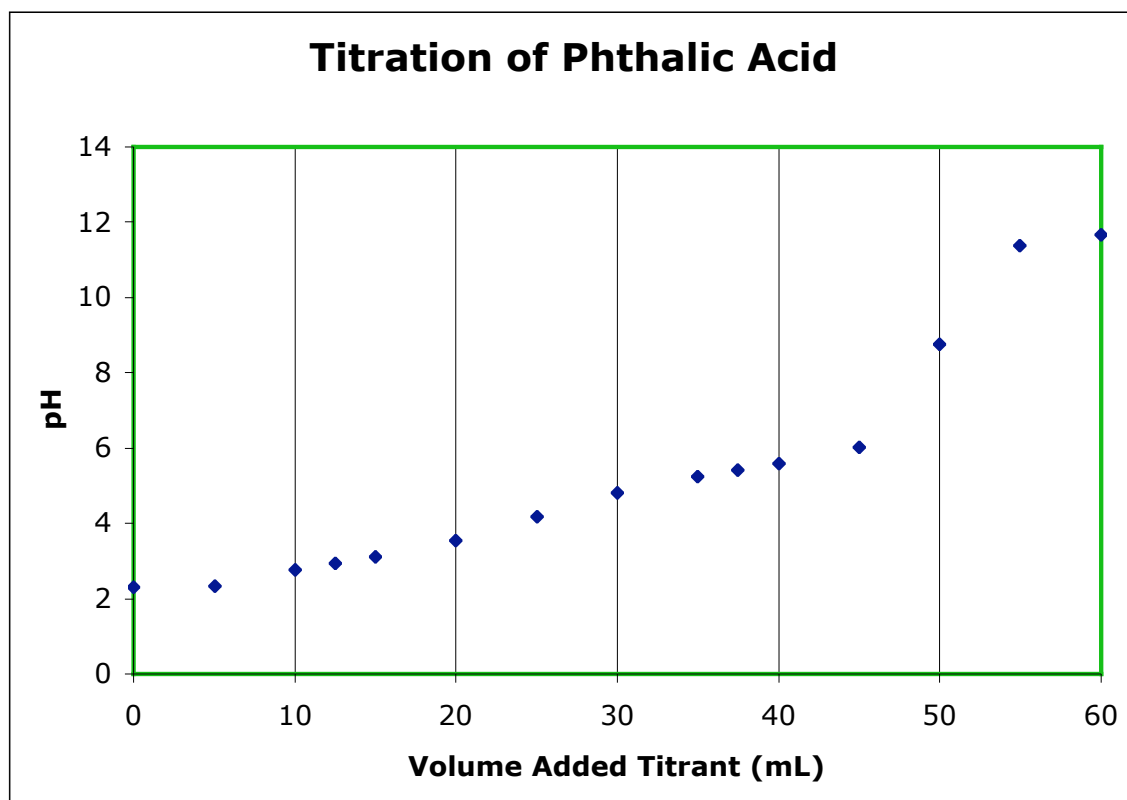
We now gather together all these data points and put them on a graph of added titrant volume vs. pH to create the titration curve.

Volume Titrant (mL)	pH
0	2.322
5	2.348
10	2.774
12.5	2.95
15	3.126
20	3.552
25	4.194
30	4.806
35	5.232
37.5	5.408
40	5.584
45	6.01
50	8.755

55 11.377

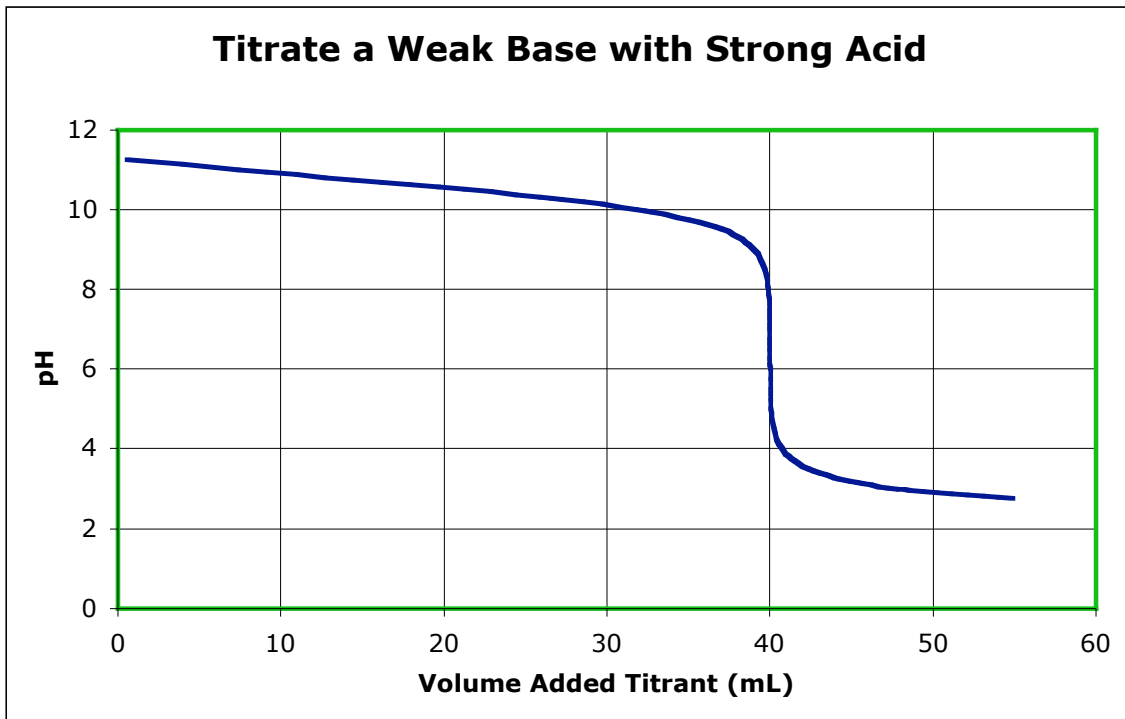
60 11.658

And the titration curve looks like

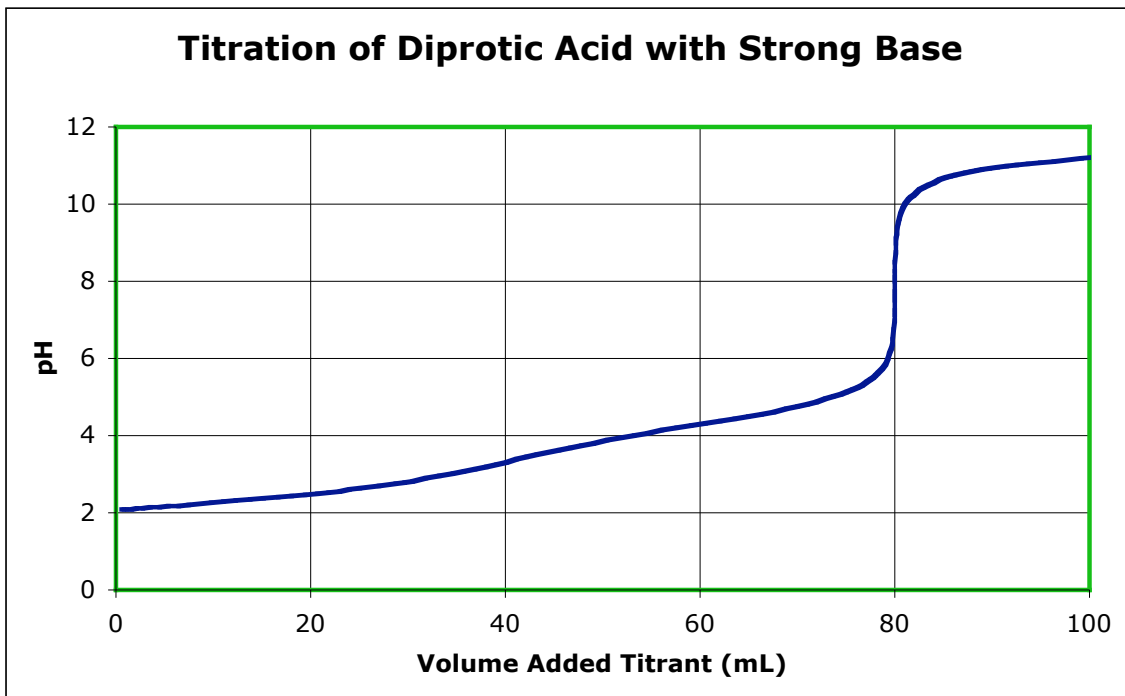


Note how the first E.P. is barely noticeable (at 25.00 mL) but the second E.P. is quite distinct and could be used to identify the titration endpoint. Under these conditions, your calculations would clearly suggest that if you were to experimentally employ this titration, you should not spend any effort in identifying the 1st E.P. but focus only on the 2nd E.P.

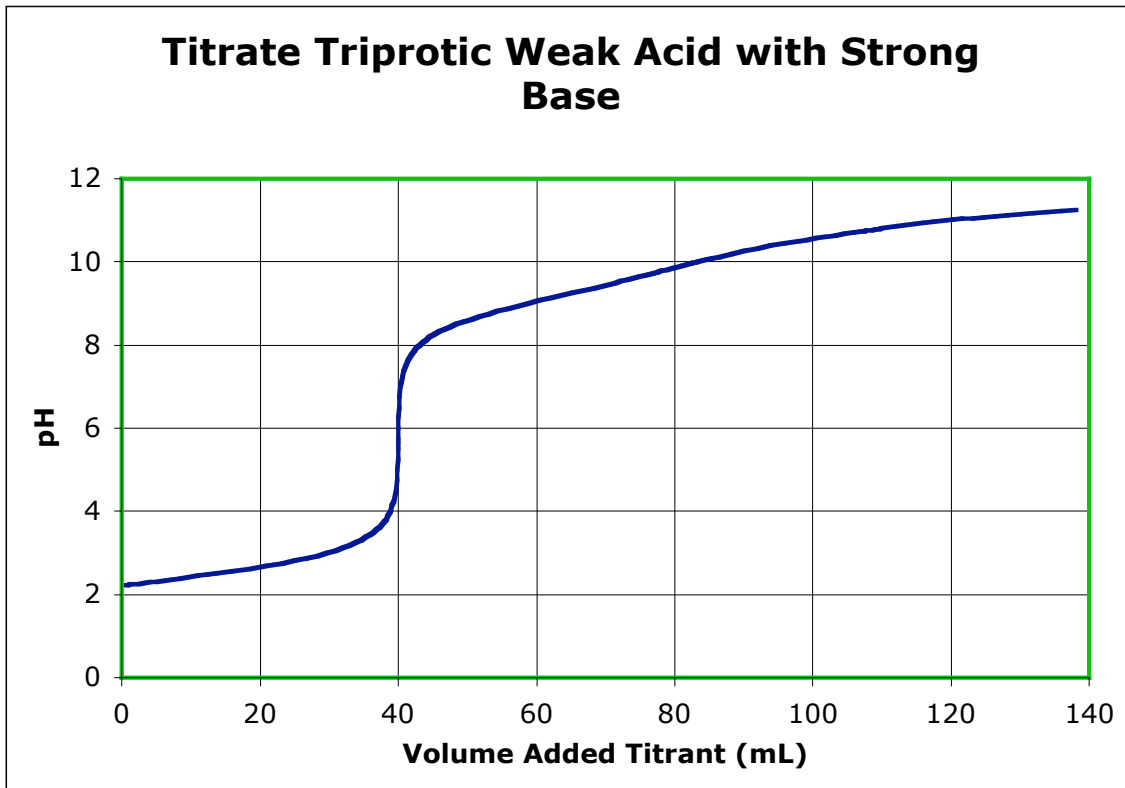
6. Here we need only to code in the correct equations from the back of chapter 12. I give here the titration curves but will also make available for download the Excel file used.
 - (a) A weak, monoprotic base titrated with a strong acid



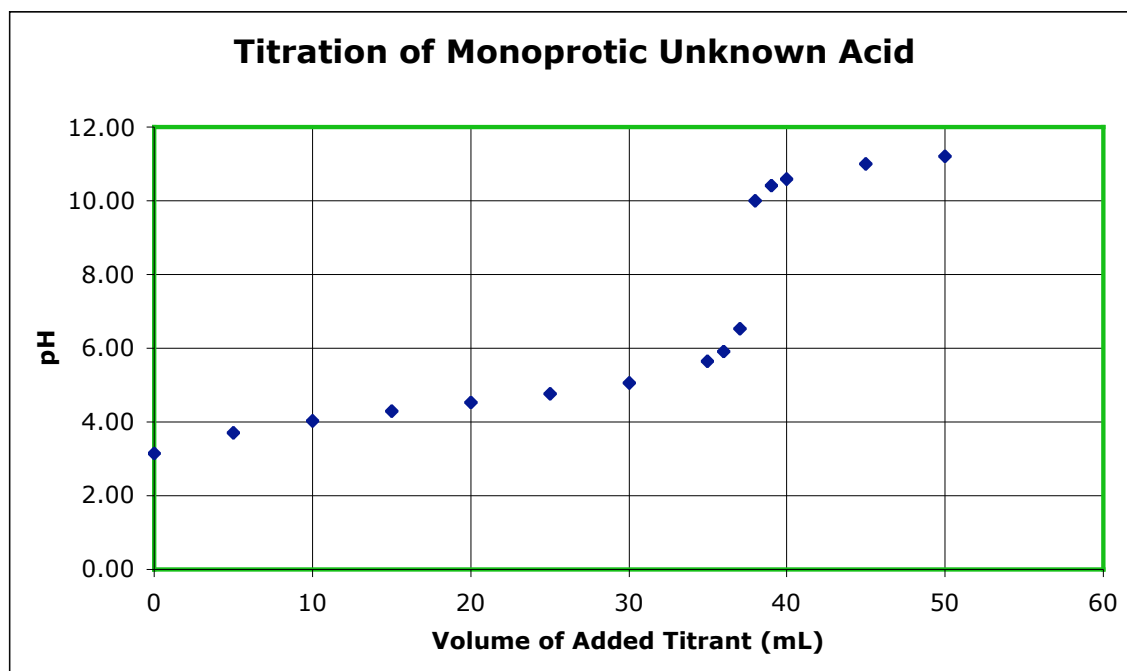
(b) A weak, diprotic acid titrated with a strong base.



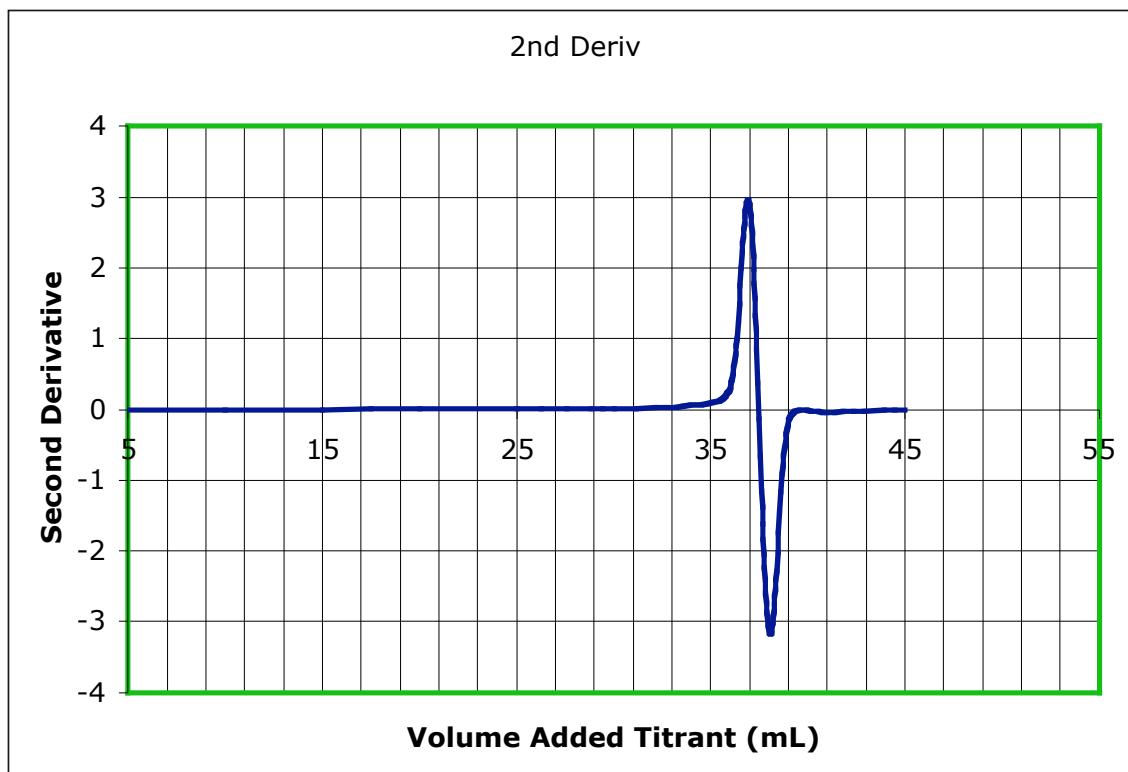
(c) Titration of a weak triprotic acid with a strong base.



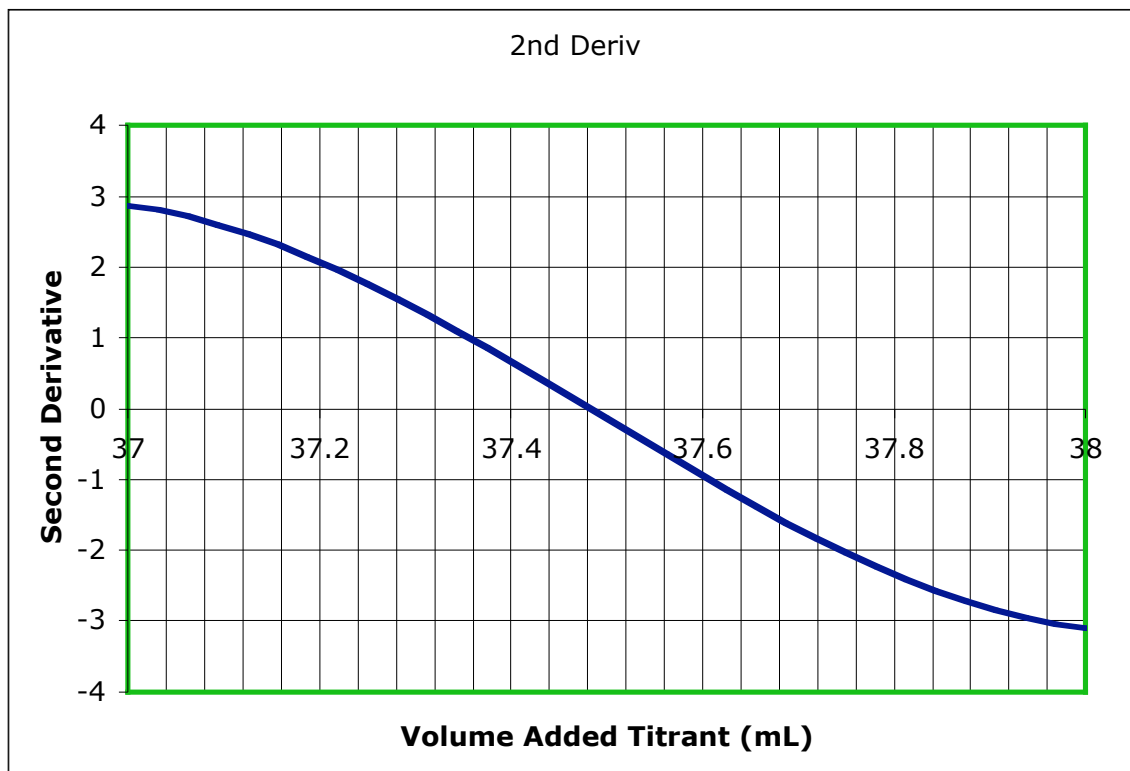
7. Here is the graph of the data. You will note that most measurements were made at intervals of 5.00 mL added titrant but near the endpoint, where the pH was changing quickly, the steps are 1 mL in size. This is, of course, to give better accuracy. But using these two techniques, we do not have to hit the equivalence point right on. First of all, here is the graph of the titration.



Clearly we will be finding the endpoint somewhere in the vicinity of 37 or 38 mL. But to get an accurate measure we take the second derivative of the data. We need to find where the data crosses zero. The first graph is the second derivative of the entire data set.



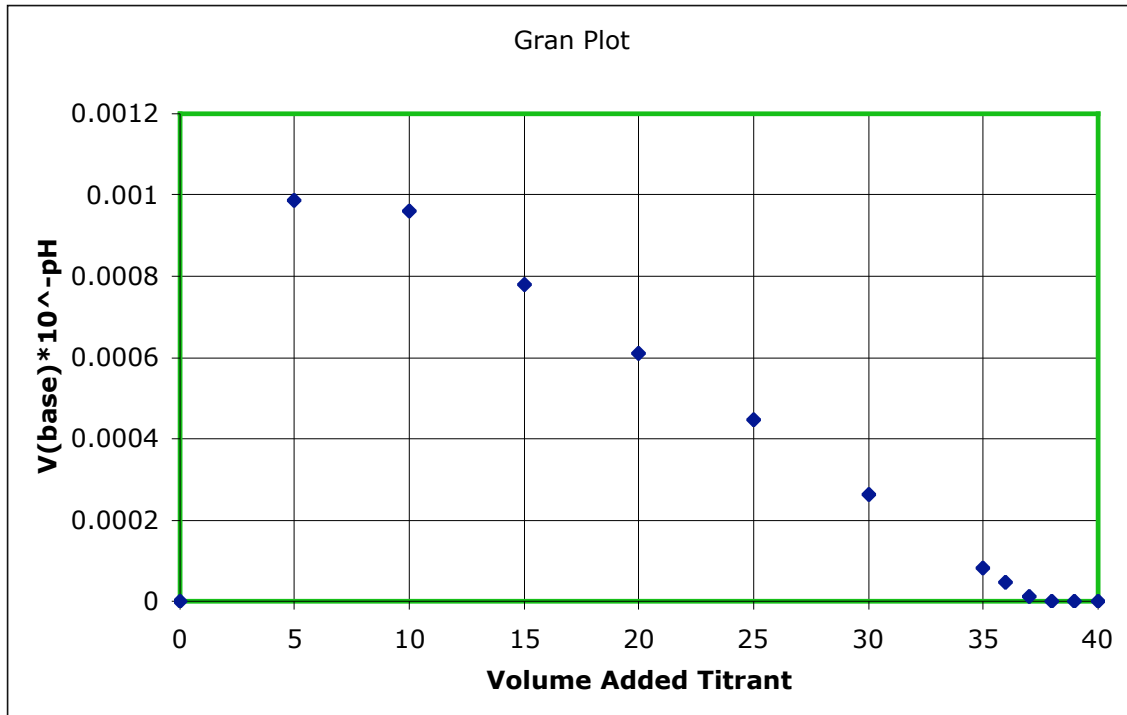
The data suggests the endpoint is just above 37 mL. We will zoom in on the graph between 37 and 38 mL.



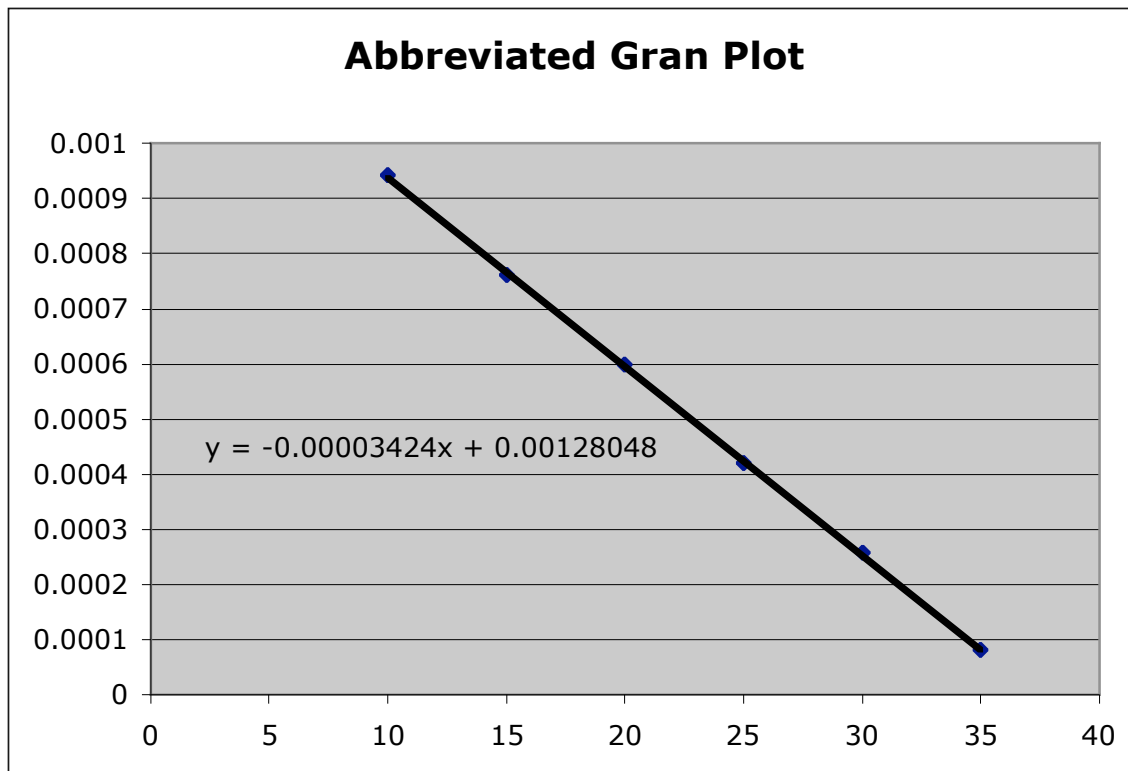
It is quite clear that the zero-crossing is at 37.44₀ mL.

Now, this endpoint depends upon the data points just around the equivalence point. The next procedure determines the endpoint but uses almost all of the titration data.

(b) The Gran plot.



This uses the Gran function on all of the data. Clearly the data beyond the equivalence point and the first couple of data points near the beginning are not valid. If we leave them out and then fit the data to a linear least squares straight line, we find



The equation of the line can be used to find the value of the x-axis when extrapolated to the zero-crossing. We just want to find the value of x when y = 0. We find

$$y = 0 = -0.00003424x + 0.00128048$$

$$x = \frac{0.00128048}{0.00003424} = 37.397 \text{ mL}$$

You can see that both are valid ways to identify the endpoint in a titration. From here you could continue to calculate the unknown concentration.