Titration of a Diprotic Acid

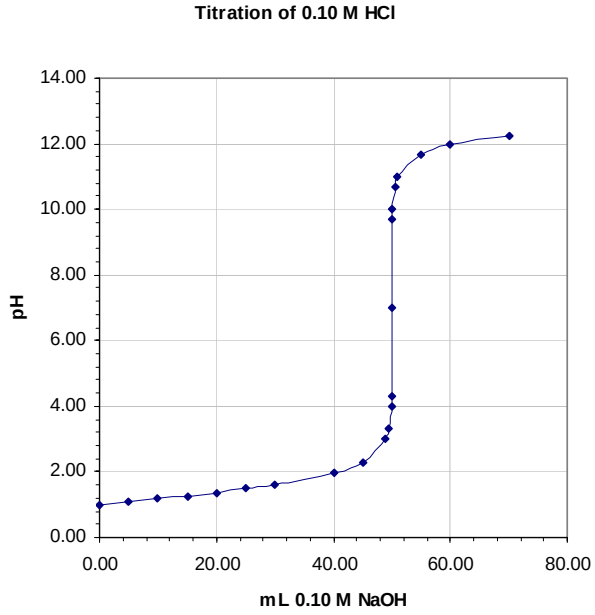
Background

Acids react with bases in a stoichiometric process we call *neutralization*. Generally the products of these reactions are some type of *salt* and water. Hydrochloric acid reacts with sodium hydroxide in this fashion:

$$HCl + NaOH \rightarrow NaCl + H_2O$$

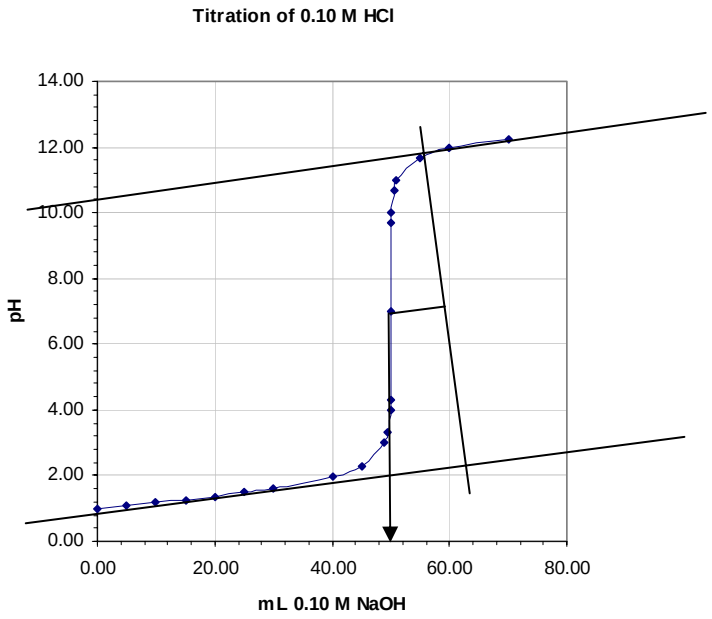
In this simple example both the acid and base are strong electrolytes and the salt produced is very soluble in water. The salt is also "neutral" since there is no tendency for the ions to accept or donate protons in the reaction mixture (i.e., no hydrolysis occurs) and thus at the stoichiometric end of the reaction (the *equivalence point*) the mixture will have a pH value of 7. The completion of the reaction can be followed with an appropriate indicator or by instrumental means such as a pH electrode.

The pH electrode is a special type of galvanic cell which is sensitive to hydronium ion concentration in solution and produces a small voltage related to that concentration. Most first-year students are familiar with the appearance of a plot of pH vs. mL of base added in a typical titration:



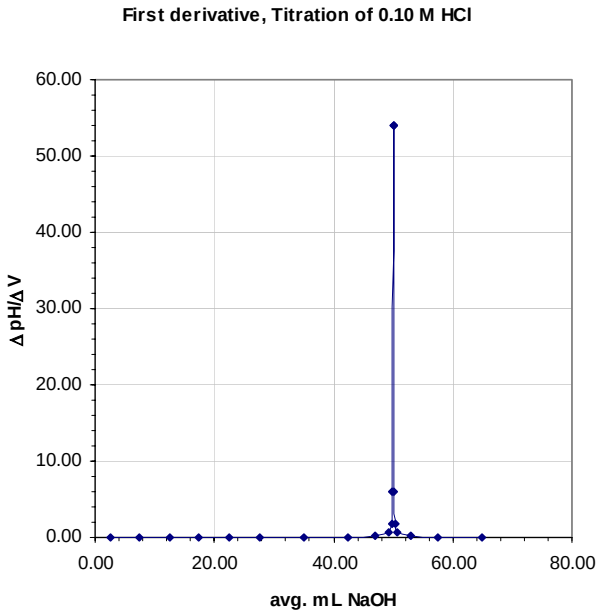
On the graph shown above the region of maximum slope is found at the volume of base which represents the stoichiometric end of the reaction or the *equivalence point*. For strong acid/base pairs this region tends to be essentially vertical and for carefully recorded data will be centered at pH 7. It is therefore often possible to determine the equivalence point volume from such a graph by a simple geometric construction as shown on the following page.

1. construct parallel tangents
2. draw perpendicular line between tangents
3. bisect line with perpendicular segment
4. where segment crosses curve, drop vertical to axis for equivalence point volume



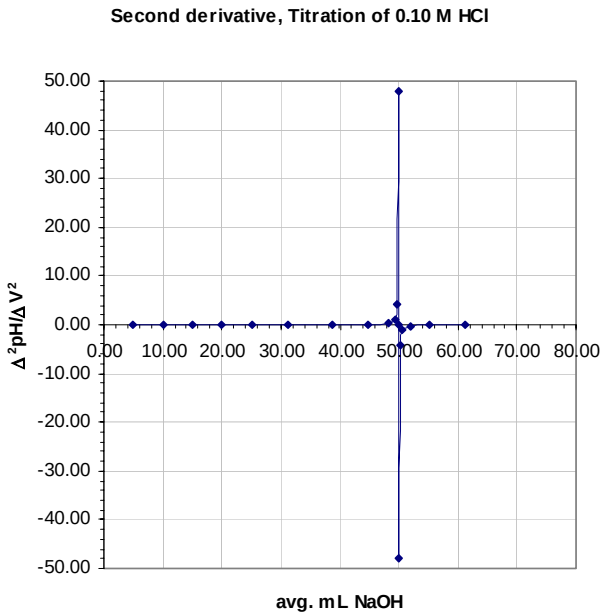
This is perhaps the simplest method for interpreting pH titration data. Because experiments do not always proceed so neatly, various other methods are often used to determine equivalence points. For example, since the region of maximum slope contains this point, a graph of the *slope* (known as a "derivative" in calculus terminology) versus the average volume for the slope interval provides a way to zero in on the desired volume. The slope could be represented as $\Delta pH/\Delta V$ (i.e., $\Delta y/\Delta x$) and the average volume as $\overline{V}$. A plot of the same data as shown earlier treated in this way is shown below:

mL NaOH	pH	$\overline{V}$	ΔpH/ΔV
0.00	1.00	-	-
5.00	1.09	2.50	0.02
10.00	1.18	7.50	0.02
15.00	1.27	12.50	0.02
20.00	1.37	17.50	0.020
25.00	1.48	22.50	0.022
30.00	1.60	27.50	0.024
40.00	1.95	35.00	0.035
45.00	2.28	42.50	0.066
49.00	3.00	47.00	0.18
49.50	3.30	49.25	0.60
49.90	4.00	49.70	1.75
49.95	4.30	49.93	6.0
50.00	7.00	49.98	54.0
50.05	9.70	50.03	54.0
50.10	10.00	50.08	6.00
50.50	10.70	50.30	1.75
51.00	11.00	50.75	0.60
55.00	11.68	53.00	0.17
60.00	11.96	57.50	0.056
70.00	12.23	65.00	0.027



Occasionally it is still difficult to judge the equivalence point even by this method. Sometimes the "peak" is rounded or has a plateau. A *second derivative* plot (the *change* in the slope) may be used in such cases. The values for the plot are obtained by operating on the first derivative data in the same way as the original data was processed. A plot of $\Delta^2 pH/\Delta V^2$ vs. $\overline{V}$ for the same titration data is shown below:

mL NaOH	pH	$\overline{V}$	$\Delta pH/\Delta V$	$\overline{V}$	$\Delta^2 pH/\Delta V^2$
0.00	1.00	-	-	-	-
5.00	1.09	2.50	0.02	-	-
10.00	1.18	7.50	0.02	5.00	0.00
15.00	1.27	12.50	0.02	10.00	0.00
20.00	1.37	17.50	0.020	15.00	0.00
25.00	1.48	22.50	0.022	20.00	0.00
30.00	1.60	27.50	0.024	25.00	0.00
40.00	1.95	35.00	0.035	31.25	0.01
45.00	2.28	42.50	0.066	38.75	0.03
49.00	3.00	47.00	0.18	44.75	0.11
49.50	3.30	49.25	0.60	48.13	0.42
49.90	4.00	49.70	1.75	49.48	1.15
49.95	4.30	49.93	6.0	49.81	4.25
50.00	7.00	49.98	54.0	49.95	48.00
50.05	9.70	50.03	54.0	50.00	0.00
50.10	10.00	50.08	6.00	50.05	-48.00
50.50	10.70	50.30	1.75	50.19	-4.25
51.00	11.00	50.75	0.60	50.53	-1.15
55.00	11.68	53.00	0.17	51.88	-0.43
60.00	11.96	57.50	0.056	55.25	-0.11
70.00	12.23	65.00	0.027	61.25	-0.03

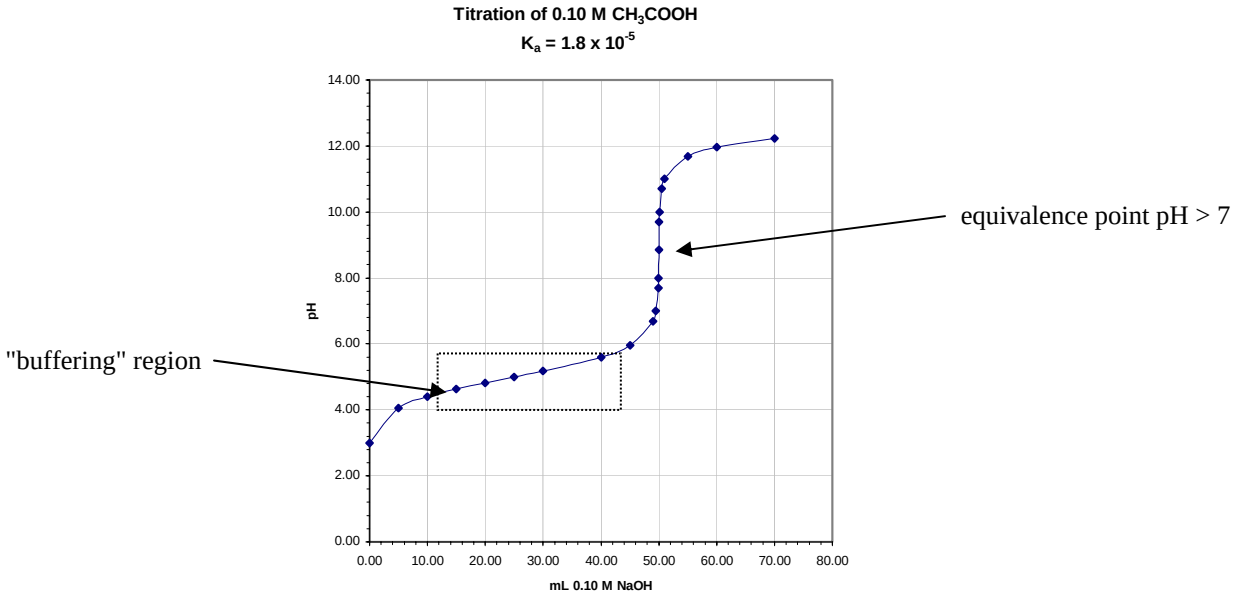


The equivalence point is found at the average volume where the function crosses y = 0. The downside to the derivative methods is that each involves a compromise in the accuracy of the volume since the interval chosen for the derivative requires an average volume. *Making the intervals small improves the accuracy and is a good reason for adding titrant in very small increments in the vicinity of the equivalence point*.

Titrations involving strong/weak pairs can be analyzed in the same way. The shape of the titration curve is somewhat altered but the general principles apply. For the reaction of a weak acid, such as acetic acid, with a strong base (like NaOH), the equivalence point pH is no longer 7 because the reaction mixture at its end contains one ion (acetate) which can accept a proton from water. This hydrolysis reaction occurs to a small extent, but that is enough to leave the reaction mixture somewhat basic at the stoichiometric end:

$$CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$$

Thus the equivalence point region on the titration curve is not centered at pH 7. There is also a more pronounced "level" region at the beginning of the titration and approaching the equivalence point as *buffering* occurs due to the partial neutralization of the acid as base is added, and the simultaneous formation of substantial amounts of conjugate base.



In addition to aiding in the location of the equivalence point, the titration graph allows the determination of the equilibrium dissociation constant for the weak component in the titration. For the example of acetic acid, this constant may be written as:

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$$

As acetic acid is neutralized, the concentration of CH_3COOH declines even as the concentration of CH_3COO^- increases---in fact their concentrations are stoichiometrically linked. *At the point in the neutralization reaction at which half of the original acid has been consumed, the amount of conjugate base produced to that point is equal to the amount of acid remaining*. This recognition results in the relationship:

$$K_a = [H_3O^+] \quad \text{or} \quad pK_a = pH$$

which is valid at the half-way point in the titration and <u>NOT</u> as a general statement. Therefore, once the equivalence point volume has been determined (by any of the methods described earlier), the pH at *half* of that volume yields information about the dissociation constant. In the "half-way" region of the titration curve the data is frequently nearly linear and a least-squares fit of that portion of the data can aid in interpretation.

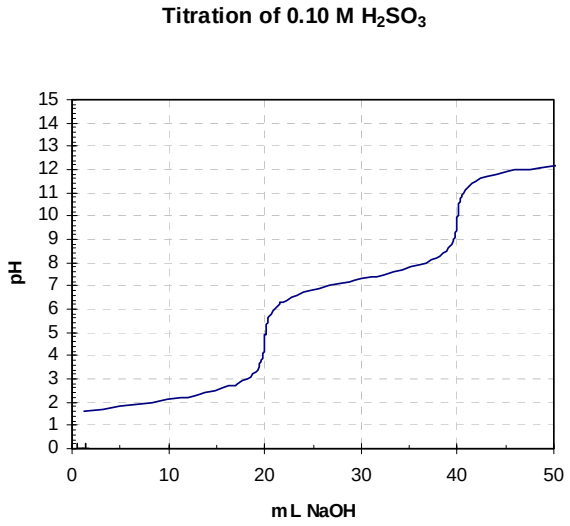
Titration data can also provide other information, of course. Since the moles of the substance are determined by the equivalence point volume it is also possible to determine the molar mass of a solid acid or base if a sample mass has been measured. This is a very typical laboratory application of the titration technique and is applicable whether the acid or base is strong or weak because it relies on the simple stoichiometry of the neutralization process.

In the examples cited so far the acids (or bases) have all been *monoprotic*, i.e., they have the ability to donate or accept only a single proton. There is only one common strong diprotic acid, H_2SO_4, but its behavior is not typical as both protons are readily donated. The weak acid *sulfurous* acid (H_2SO_3) is much more typical. Sulfurous acid dissociates in two steps:

$$H_2SO_3 + H_2O \leftrightarrows HSO_3^- + H_3O^+ \qquad K_1 = 1.4 \times 10^{-2}$$

$$HSO_3^- + H_2O \leftrightarrows SO_3^{2-} + H_3O^+ \qquad K_2 = 6.5 \times 10^{-8}$$

For any similar system the dissociation constants are always in the relationship $K_1 > K_2$. In the case of sulfurous acid--and many others--the K values are sufficiently different that the mixture behaves during titration as though there were two acids present, but not simultaneously. Because K_2 is much smaller than K_1 there is essentially no SO_3^{2-} present in the mixture until all of the H_2SO_3 has been converted to HSO_3^-. This would show up on a titration curve as an equivalence point. Then the "second" titration would begin with the HSO_3^-, giving a second equivalence point at the stoichiometric end of the neutralization reaction. Such a titration would give a curve as shown below:



For weak diprotic acids in which K_1 is about 10^4 times (or more) greater than K_2 the relationships outlined for the monoprotic example are essentially valid but perhaps not as obvious. For the general case of H_2A titrated with NaOH, the neutralization reaction could be written as:

$$H_2A + 2\ NaOH \rightarrow Na_2A + 2\ H_2O$$

At the second equivalence point the moles of base added are *twice* the moles of acid present. Thus the moles of acid can be determined either by dividing these moles by two or by simply using the *half-way volume* in the titration. At that point the "first" neutralization is complete:

$$H_2A + NaOH \rightarrow HA^- + H_2O$$

and moles of base added do indeed equal the moles of acid originally present. With a corresponding sample mass, the molar mass may then be determined.

The K values for a weak diprotic acid may be determined by observing that when the value for the second dissociation is much smaller than that for the first, the first dissociation is the only one of any significance as long as some of the diprotic species is present. Halfway to the <u>first</u> equivalence point, half of the H_2A has been converted to HA^- while hardly any HA^- has dissociated. Therefore an analysis similar to that used for the monoprotic case can be used. *At half-way to the first equivalence point, the concentrations of H_2A and HA^- are equal*:

$$K_1 = \frac{[HA^-][H_3O^+]}{[H_2A]}$$

and therefore $K_1 = [H_3O^+]$ OR $pK_1 = pH$

Once the first equivalence point has been reached, the important equilibrium in the mixture becomes:

$$HA^- + H_2O \leftrightarrows A^{2-} + H_3O^+$$

since the only acid species present is HA^-. K_2 is therefore:

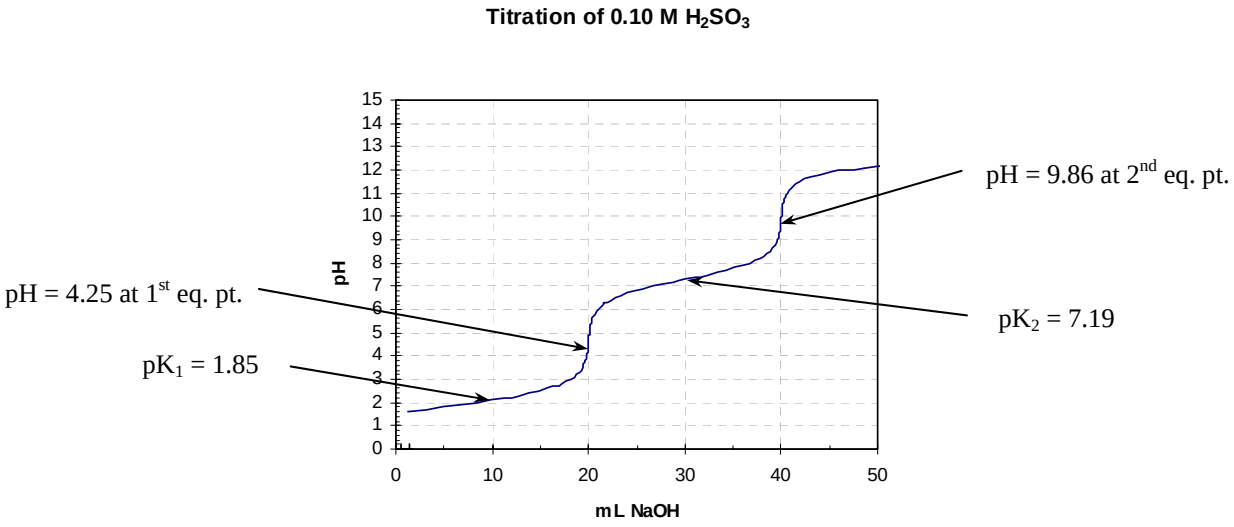
$$K_2 = \frac{[A^{2-}][H_3O^+]}{[HA^-]}$$

Proceeding on the assumption that $K_1 >>> K_2$, the mixture now behaves as if a monoprotic acid, HA^-, is being titrated. Therefore *half-way from the first equivalence point* (which is the beginning of this "second" titration) *to the second or final equivalence point, half of the HA^- will have been converted to A^{2-}* and thus:

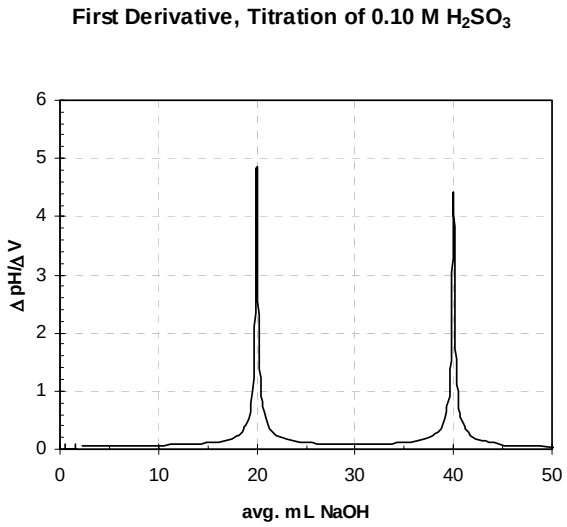
$$K_2 = \frac{[A^{2-}][H_3O^+]}{[HA^-]}$$

so $K_2 = [H_3O^+]$ OR $pK_2 = pH$

Which is, once again, <u>not</u> a general statement but is applicable to this situation for the reasons discussed above. A summary of these relationships is shown below with reference to the titration of 20 mL of 0.10 M H_2SO_3 with 0.10 M NaOH.

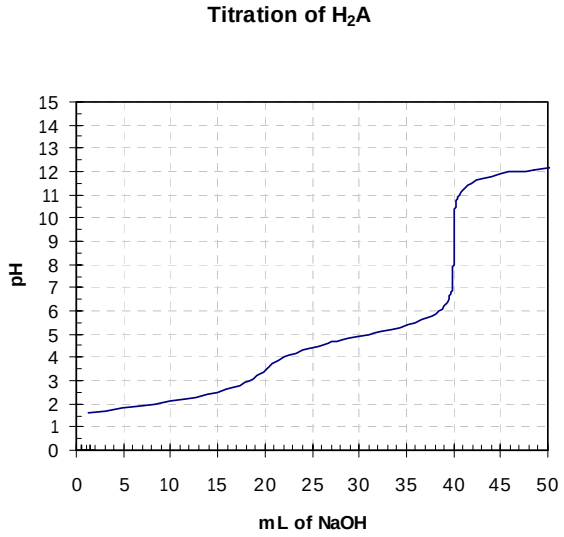


The first derivative of the titration curve on the previous page makes clear that data processing similar to that for a monoprotic acid can be applied to diprotic acid titrations as well:



There are a few additional relationships at various points in the titration which are not necessarily obvious and while they are not strictly necessary for the determination of the K values, they do provide alternate ways of getting the information and thus can sometimes be helpful in tracking down errors or "improving" results if one equivalence point appears more accurate than the other.

A careful titration will generally yield an excellent *final* equivalence point. This can be checked against the known molar mass of the (solid) acid. If the two K values are not as far apart as in the ideal case, the *first* equivalence point is sometimes quite gradual and therefore difficult to discern from a graph, as seen in the example below:



However, since the neutralization is stoichiometric, *the half-way point in the titration of a diprotic acid must be half of the volume for the final equivalence point*. Similarly, the other "half-way" points (actually, one-fourth and three-quarters through the titration) must also be related to the final equivalence point volume in a simple fractional way.

One additional relationship involving K_1 and K_2 may be derived by making a few appropriate assumptions about the titration mixture <u>at</u> the first equivalence point. Suppose the hypothetical acid H_2A has $K_1 = 10^{-3}$ and $K_2 = 10^{-7}$. At the first equivalence point the predominant acid species in solution is HA^-. This species may take part in three competing equilibria:

$$2\ HA^- \leftrightarrows H_2A + A^{2-} \quad \text{[disproportionation]} \quad K = \frac{K_2}{K_1} = 10^{-4}$$

$$HA^- + H_2O \leftrightarrows H_2A + OH^- \quad \text{[hydrolysis]} \quad K = \frac{K_w}{K_1} = 10^{-8}$$

$$HA^- + H_2O \leftrightarrows H_3O^+ + A^{2-} \quad \text{[dissociation]} \quad K_2 = 10^{-7}$$

The values for the equilibrium constants indicate that only the first reaction is significant, i.e., $[H_2A] \approx [A^{2-}]$. Both of these terms appear in the overall K for the dissociation of H_2A:

$$K = K_1 \times K_2 = \frac{[H_3O^+]^2[A^{2-}]}{[H_2A]}$$

and therefore AT THE FIRST EQUIVALENCE POINT:

$$K_1 \times K_2 = [H_3O^+]^2 \quad \text{or} \quad pK_1 + pK_2 = 2pH$$

Finally, a few words need to be said about the potential accuracy of titrations for the determination of K values. Given even the best of conditions (e.g., with $K_1 >>> K_2$), it is often very difficult to obtain handbook values. The assumptions inherent in the simple treatment of the data are part of the problem. The two acid forms are not *completely* independent.

A more subtle factor which will be discussed at greater length in the experiments that follow this one is the <u>non-ideal behavior of the solution mixture</u> at any given point in the titration. We assume that only certain ions are present and that these ions do not interact with one another. In fact, ion interactions are common at the concentrations typical in these titrations and they generally have the effect of making ion concentrations appear <u>lower</u> than they actually are, the effect being more pronounced for ions of higher charge. This affects the pH values, but not in a simple way as an appropriate "correction" involves consideration of the ions present, their concentrations *and* their charges. There are mathematical models for treating titration data which address these realities but they are beyond the scope of our experimental work in this course.

The Experiment

There is one part to this experiment:

- titration of a 20 mL sample of diprotic acid solution

The following non-locker materials will be provided:

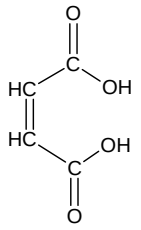
- 100 mL volumetric flask
- CBL w/pH electrode, amplifier and power supply
- pH 4 and 10 buffers
- 20 mL pipet w/large bulb
- approx. 0.1 M NaOH [record exact concentration]

The Chemicals

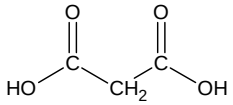
Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

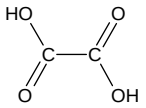
Maleic acid ($C_4H_4O_4$) or *cis*-butenedioic acid is a white, crystalline solid with an acidulous odor and repulsive taste. It can be converted to fumaric acid (*trans*-butenedioic acid) by heating. It is used in the manufacture of artificial resins, for retarding the rancidity of fats and in the dye industry.

maleic acid 

Malonic acid ($C_3H_4O_4$) or propanedioic acid is very soluble in water (1 g/0.65 mL) and is used in the manufacture of barbiturates. It is a strong irritant.

malonic acid 

Oxalic acid ($C_2H_2O_4$) or ethanedioic acid is present in many plants and vegetables, particularly those of the *Oxalis* and *Rumex* families. The acid is used as a general analytic reagent as well as in the dye industry, for bleaching wood, in ceramic pigments and in the paper industry. The solid is caustic and corrosive. Ingestion may cause severe gastroenteritis. Severe poisoning can end fatally.

oxalic acid 

Technique Discussion

Many titrations are now done automatically by instruments which are calibrated to deliver small increments of titrant between pH measurements. When such equipment is lacking, the well-trained hand is still an important tool. You should strive to develop good control of the buret stopcock, delivering single drops with 100% reliability and no false squirts. Accurately reading the volume on the buret is another important skill. Be sure the meniscus is at eye-level when you record a volume. Many people find it helpful to place a card behind the buret with a white/black boundary to help determine the exact position of the meniscus.

A word or two needs to be said about the care and handling of a modern pH electrode. Most of the electrode is made of plastic and it is difficult to damage except at the business end. There, it is fragile and sensitive to abrasion. The electrode should never be allowed to dry out and should never be placed in distilled water or strongly basic solutions for extended periods of time. It is stored in a special salt solution. When you are ready to use it, you rinse off the solution with distilled water, pat dry gently with a Kimwipe and immerse the electrode in the solution you are measuring. Swirling it around (in a calibrating buffer, for example) is not a bad idea to help speed equilibration. But do not knock it carelessly against the glass or allow a stirring bar to bang into it. When you are finished using the electrode, rinse it with distilled water again, dry gently and replace it in its storage solution.

A sample of your assigned solid diprotic acid should be measured out on the analytical balance. Any amount in the range of 1.12-1.20 g will ensure that no more than 50 mL of NaOH will be required for the titration. The solid sample is then transferred *quantitatively* to the 100 mL volumetric flask. Quantitative transfers of water-soluble solids are usually accomplished by dissolving (or mostly dissolving) the solid in a small amount of water. This mixture is then transferred carefully. Additional water--in small amounts--is used to repeatedly rinse the original container (and/or complete dissolution) and continue the transfer. The object of the repeated rinses is to be sure ALL of the original material is rinsed into the destination container (in this case, the volumetric flask). Of course no amount of repeated rinsing will do any good if material is spilled or otherwise lost, so take your time. **Final dilution to the mark should not occur until the solid is completely dissolved.**

20 mL of this solution should be pipetted into a 250 mL beaker (rinse the pipet with a little of the solution first--discard the rinse). Prepare a buret by rinsing with a small amount of the NaOH solution (discard rinse) and then filling it to the 0.00 mL mark.

Calibrate the pH electrode using buffers at pH 4 and pH 10. You will be using the CBL units to measure pH so **be sure to bring your TI-83/P calculator to lab and have the HCHEM.83G programs in memory**. Once the electrode is calibrated, set up the calculator to measure pH VS. USER X (volume) and use the GRAPHICAL option. YMAX and YMIN can be 14 and 0, respectively. XMAX and XMIN should be 50 and 0.

Place the electrode in the solution. You can let the electrode rest on the bottom of the beaker if you like but be sure that the magnetic stirring bar will not hit the electrode as it turns. Add enough distilled water to cover the bottom of the electrode with solution. Stir *moderately* fast.

The titration should be performed carefully with the object of obtaining a pH change NO GREATER than 0.25 units by adding base from the buret. At the beginning of the titration this may take a considerable amount of base [**look back at the titration curves**] and very little near the equivalence points. The buret has divisions of 0.1 mL so the smallest amount that you can add reproducibly is 0.05 mL. Greater precision than this is not justified in an experiment of this sort.

It should go without saying that for such a careful technique the "milk-cow" method of titration will not suffice. You must have very good control over the stopcock and keep your wits about you. If you turn it the wrong way during the equivalence point region it's all over.

The titration should continue until the second equivalence point has been passed and the titration curve is beginning to level out once again. Ending prematurely may make the derivative calculations less than satisfactory.

The Report

Your initial calculations should include:

[this entire section must be done on a spreadsheet]

1. A graph of pH vs. mL of NaOH added

2. A table of ΔV, ΔpH, $\Delta pH/\Delta V$, and $\overline{V}$ (the average volumes of NaOH for the derivative intervals) [required only for the endpoint regions of the titration but you may do more if you wish]

3. Graphs of $\Delta pH/\Delta V$ vs. $\overline{V}$, expanded to show endpoints accurately

4. The values of K_1 and K_2

5. The molar mass of the acid based on the total volume of NaOH added at the second equivalence point [remember…..you only used 20 mL of your 100 mL solution]

6. A possible identity of the organic diprotic acid [relative error on the molar mass] (try the CRC under *dissociation constants for organic acids*)

Your conclusion to this experiment should include a comparison of your results to the values given for the acid you select. For an experiment of this type it is usual for one of the K values to be more accurate than the other. Speculate on why this is so. Investigate some of the alternative methods for obtaining the K values as described in the Background discussion. Is there a "best" way for your data?