**Generating a Titration Curve to Determine $K_a$ for an Acid**  
(and practicing titration calculations)

**Goals:**
1. Generate a titration curve for a weak acid, and then use it to determine the $K_a$ for the acid.
2. Calculate theoretical values of pH at various points (using $K_a$) and compare to experimental values.

**I. Introduction.**

For a titration of an acid with a base, a *titration curve* is a plot of pH versus "Volume of base (solution) added". The initial pH will be significantly less than 7 in this case for any significant initial concentration of acid, and as NaOH is added, the pH will increase since OH" is a basic species. However, the shape of the curve is certainly not linear. The pH initially increases somewhat rapidly, but then "flattens out" for awhile, and then increases fairly abruptly later on, and then ultimately flattens out again. This dependence is a result of the [H$_3$O$^+$] being related to the concentrations of HA and A$^-$ according to the acid ionization equilibrium equation and corresponding $K_a$ expression:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \Rightarrow [H_3O^+] = K_a \frac{[HA]}{[A^-]} \Rightarrow pH = pK_a + \log \frac{[A^-]}{[HA]} \quad (1)$$

Each point in the titration curve corresponds to a different amount of NaOH added. As NaOH is added, OH$^+$ reacts with HA to form A$^-$: HA + OH$^-$ → A$^-$ + H$_2$O (the "titration reaction"; $K_{\text{tit}} \gg 1$). As HA is converted to A$, the ratio [HA]/[A$^-$] varies, and so the pH varies (See (1)). When either [HA] or [A$^-$] is very small, a small change in its concentration will lead to a sizable change in the ratio [HA]/[A$^-$], and that leads to a sizable change in pH. When both [HA] and [A$^-$] are not very small, a small change in either one’s concentration does *not* change [HA]/[A$^-$] very much and so the pH does not change much. That is why the curve is steep at the beginning (when [A$^-$] is very small) and at the *equivalence point* (when [HA] is very small), but is fairly "flat" in between (in the "buffer region", where significant amounts of both HA and A$^-$ are present). The "flattest" point of the curve is at the *half-equivalence point*, where moles of HA = moles of A$^-$ (since both equal half of the initial moles of HA), and thus [HA] = [A$^-$]. Inspection of (1) shows that the half equivalence point is also special in that it is the point at which [H$_3$O$^+$] = $K_a$ (because if [HA] = [A$^-$], then [HA]/[A$^-$] = 1) and thus pH = p$K_a$. See Figure below:

In summary, one can determine the $K_a$ for an acid by simply measuring the pH of a solution of the acid as incremental amounts of a solution of NaOH (or other strong base) are added. Once a plot of pH vs. "volume of base added" is made, one can find the equivalence point volume first, by finding the steepest part of the curve (other than the beginning). Then one can take *half* of that volume to get a precise value for the *half* equivalence point (which one could locate approximately as well by looking for the flattest point on the curve), read off the pH value there to get the value of p$K_a$ of the acid, and then convert p$K_a$ to $K_a$. After $K_a$ is determined, I’ll have you use your [HA]$_o$ value and [NaOH]$_{\text{titrant}}$, along with the $K_a$, to calculate (predict) pH values at selected points to compare with experiment.
II. Prelab (Practice in interpreting titration curves)
1. For each titration curve, find (be precise in a & b!):
   a. The equivalence point volume and pH.
   b. The half equivalence point volume and pH.
   c. The $K_a$ of the acid being titrated.
2. Which acid is the weaker acid? How do you know?
3. Which sample had more moles of HA in it initially? Give reason!
4. Do the prelab calculation found in part IIIA below.
5. Calculate the (expected) initial concentration of your acid solution (see Part IIIB below to get the initial volume of your acid solution).

III. Experimental Information and Procedures
A. Background and preliminary calculation. You will be given access to one of the following four acids:
   (i) Mandelic Acid ($C_6H_5CH(OH)COOH$; 152.16 g/mol); (ii) Glycolic Acid (CH$_2$(OH)COOH; 76.05 g/mol);
   (iii) $\text{KHC}_8\text{H}_4\text{O}_4$ (an acidic salt; 204.23 g/mol); (iv) $\text{NaH}_2\text{PO}_4\cdot\text{H}_2\text{O}$ (an acidic salt; 138.0 g/mol)

   You will be preparing a solution containing your acid, and then you will titrate that solution with a standardized solution of approximately 0.1 M NaOH ("standardized" means that its concentration is known with great accuracy and precision; record the value from the NaOH(aq) reagent bottle).

   Prelab Calculation: Given the molar mass of your acid (just pick one), calculate the number of grams of the acid needed to just react with 30.0 mL of 0.100 M NaOH.

   Now, given what you just calculated, if you were to start with that number of grams of acid in a titration, at what "volume of titrant added" would you expect to reach the equivalence point if the titrant used were 0.100 M NaOH? (Note this is NOT a trick question, I just want to make sure you understand what the meaning of "equivalence point" is in a titration!) I hope that you realize that the answer to this question is "30.0 mL!" Please ask me if you don’t understand this.

B. Preparation of the acid solution.
1. TARE a clean and dry 100-mL beaker on the balance (i.e., put the beaker on the pan and press the TARE button; the reading should go to 0.000 g), and then weigh out the number of grams of your acid that you calculated in part A into the beaker (to within 0.01 g of what you calculated; do not waste time trying to get it to match more precisely than that).

2. Add 40.0 mL of deionized water using a graduated cylinder, and swirl to dissolve all of the solid.

3. Add a magnetic stir bar, and possibly a few drops of an acid-base indicator (optional; ask me).

C. Titration of the acid solution.
1. Basic ideas and Setup.
   a. You will be adding NaOH solution (titrant) in small aliquots (from a buret) to your acid solution and measuring and recording the pH after each addition of titrant. Once you are finished with the titration (as indicated below), you will plot "pH vs. volume of titrant added (in mL)", so make sure you have plenty of room on a separate sheet of paper to record your values of "volume of titrant added" and corresponding pH (make a table, with headings; THIS TABLE WILL BE HANDED IN). You should also write down the concentration of the NaOH solution from the bottle at this point. Obtain approximately 75 mL of the titrant (NaOH) solution in a clean and dry 150 mL Erlenmeyer flask (Note: It is always a good idea to swirl the reagent bottle of a standardized solution before removing any solution). Place a watch glass on this flask when not pouring from it.

   b. Buret Prep. Before the titration, prepare the buret by doing the following: 1) Make sure that the stopcock is firmly seated in the end of the buret! There are two types of tips, and if you have the wrong one inserted, it could fall out when you start turning the stopcock! 2) Rinse the buret with 2 or 3 portions of ~3 mL of the titrant (NaOH) solution (as I’ll demonstrate). 3) Attach the buret to a buret clamp on a ring stand, and fill the buret to above the 0.00 mL line with titrant. 4) Bring the
level down to 0.00 mL by draining out the appropriate amount via the stopcock (strictly speaking
you need not start at precisely 0.00 mL, but when making a titration curve, it is very convenient to
do so because then your volume READINGS will equal your "volume added").

c. Stir plate/pH electrode/buret setup. You will find the pH electrode immersed in a buffer solution
"plug". Remove it carefully from that solution (keeping it upright at all times) and rinse it with some
deonized water from your wash bottle. Put the plug in a safe place (you'll need to replace it after
the experiment!). Carefully remove excess water from the electrode by lightly blotting (NOT
"wiping") the tip with a tissue (Kimwipes). Calibrate the pH electrode using two buffers at specific
pH values (7.00 and 4.00). Place and center your beaker of acid solution on a stir plate, and get
your stir bar spinning at a reasonable rate by adjusting the "stir" knob on the stir plate (the knob is
very sensitive!) Once you get the stir bar spinning, never touch the knob again (unless of course
the bar stops spinning)--just let it stir constantly throughout the entire experiment.

Now lower the pH electrode (on the support arm holder) into your solution (in the 100 mL beaker)
such that the tip is completely submerged, but the bottom of the tip is above the level of the top of
the stir bar. The electrode need NOT be centered in the solution; it can be anywhere as long as the
tip is submerged. Move the ring stand with the buret so that the buret tip is over the 100 mL
beaker, AND in a place such that you can access the stopcock. Lower the buret so that the tip is
below the rim of the beaker, but well above the liquid level. You may need to adjust the position of
the pH electrode and buret stand to get things to "fit" okay (you may also need to rotate the buret
clamp on the ring stand to get things to work out; ask me). You are now ready to begin!

2. The titration.

Note: Remember that you should know approximately where to expect your equivalence point, and
thus your half e.p., (look closely at the calculation in III A)! Use this to help you gauge "where
you're at" in the titration (see below). ALSO: your goal is not to stop when you reach the
equivalence point!!! This is not a standard "titration"—you want to generate a full "curve".

First measure and record the pH of your solution BEFORE adding any NaOH solution (volume
added = 0.00 mL). Then add ~2 mL and record the new buret reading (precisely!) and the
_corresponding pH. You will need to hit “READ” each time that you want to make a new reading.
Then add another ~2 mL, and so on, recording the pH values and buret readings each time. As you
get closer to the equivalence point, you will need to add smaller and smaller amounts of
NaOH or else you will likely “miss” the equivalence point. Note that your change in pH after
each 2-mL addition will initially be sizable (> 0.5 pH unit), then it should get smaller as you approach
the half-equivalence point (ΔpH probably ≤ 0.1 pH unit around middle of buffer region), and then it
will begin to get larger again as you approach the equivalence point. As a guideline, after you’ve
passed the half-equivalence point, when a pH reading is more than about 0.25 pH units higher than
the previous reading DO NOT ADD ANOTHER 2-mL aliquot! You do not want to "miss" the
equivalence point, right? (Why not?) At this point, add titrant more judiciously, perhaps in 0.5 mL
increments at first, while closely monitoring the increase in pH with each addition. If the pH
increases by more than 0.2 units after an addition try making additions dropwise, and only record the
buret reading and pH when the pH is about 0.2 units above your last reading. Keep making
dropwise additions through the equivalence point--until it seems to take multiple drops to get a pH
increase of 0.2 units. At this point, you can start making progressively larger additions again since
the pH will begin to get less sensitive to additions of titrant. Ultimately make at least FOUR 2-mL
additions AFTER you see the pH reach about 11.5. (Please ask me to confirm before you "stop"!)

When you are done, remove the electrode, rinse it with deionized water, and put it back into the
buffer solution it was in originally. Carefully dump the titrated solution down the drain, making sure
to recover the stir bar and return it. Rinse any unused titrant down the drain as well, and rinse the
buret with deionized water before returning it.

D. Raw Data “Format”. Plot your pH/Volume raw data in Excel using an X-Y scatter plot (NOT a “line
plot!”). Make sure you plot pH (y-axis) vs. Volume (in mL) of NaOH solution added (x-axis).
Report Form: Acid Titration Curve

Name(s): ____________________________

I. Raw Data (and assumed quantities)

Name of Acid (or Acid Salt): ____________________ Volume of water used to dissolve acid: ________

pH and “Volume of NaOH(aq) added” values: Attach table of raw data and plot (titration curve).

[NaOH]_{t} = ___________ (Assumed quantity; this is not raw data because it wasn’t measured by you)

II. Data Analysis and Calculations

1. (a) Use your plot, your raw data table, and definitions from class to determine the following as precisely as your data allow:

\( V_{ep} \) (V at equivalence point) = ______ pH at equivalence point: ______

\( V_{1/2 ep} \) (V at half-equivalence point)\(^1\) = ______ pH at half-equivalence point: ______

\( pK_a \) of acid (from experiment): ______ \( K_a \) of acid (from experiment): ______

(b) Find a published \( pK_a \) value (or find a \( K_a \) value and calculate the \( pK_a \) yourself) for your acid (check your book’s appendix, the CRC handbook, or another reference provided). Comment on the agreement between your value and the published one. Suggest ideas why the values might not be identical.

\( pK_a \) of acid (published value): _______ Comments:

Source: ___________________________

2. (a) initial moles of acid = ________ (Do NOT use mass and molar mass here! Use the titration!)

Show calculation:

initial concentration of acid ([acid],o) = ________ Show calculation:

(b) Using YOUR experimental \( K_a \) value (and other "amounts" from above, as needed) calculate a value for what the pH "should" be (according to theory) at the following points:

(i) at the beginning of the titration.

\( \text{Use back of page to show calculation; copy the result here: } \) _______ (theoretical)

\( \text{actual pH at beginning of titration (from raw data): } \) _______ (experimental)

Comment on the agreement between the calculated and experimental values.

(ii) at the equivalence point.

\( \text{Use back of page to show calculation; copy the result here: } \) _______ (theoretical)

\( \text{actual pH at equivalence point (from raw data): } \) _______ (experimental)

Comment on the agreement between the calculated and experimental values.

(iii) after 20.0 mL of titrant were added

\( \text{Use back of page to show calculation; copy the result here: } \) _______ (theoretical)

\( \text{actual pH after 20.0 mL of titrant added (from raw data): } \) _______ (experimental)

Comment on the agreement between the calculated and experimental values.

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Note: If values are not within 1 pH unit of one another (and often much closer), check your calculations!

\(^1\) Interpolate, if necessary!! Ask me if you do not know how to do an interpolation.