Identification of a Polyprotic Acid

Objective:

Determine the identity of an unknown polyprotic acid.

Background:

Using a titration curve and the Henderson-Hasselbalch equation, it is possible to determine the pK_a value of an acid.

Consider the Henderson-Hasselbalch equation:

$$pH = pK_a + \log([A^-]/[HA])$$

If $[A^-] = [HA]$ then the ratio $[A^-]/[HA] = 1$. Putting this value into the Henderson-Hasselbalch equation one gets:

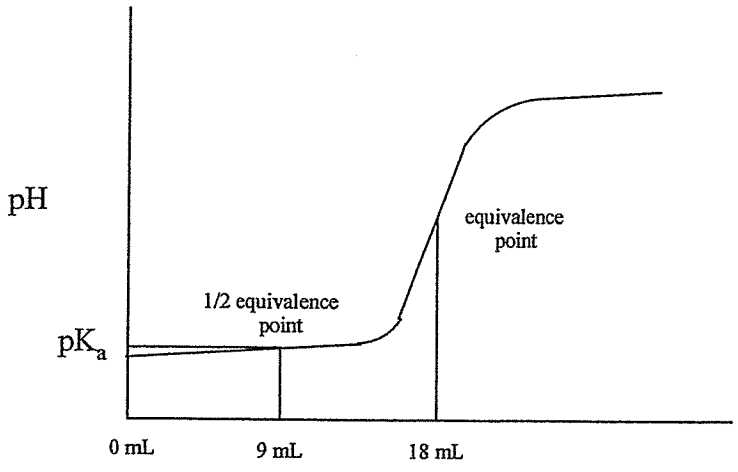
$$pH = pK_a + \log(1)$$
$$pH = pK_a + 0$$
$$pH = pK_a$$

Therefore, when $[A^-] = [HA]$, the pH of the solution equals the pK_a of the acid.

Consider the titration reaction:

$$HA + NaOH \longrightarrow H_2O + A^-$$

At the equivalence point, all of the HA has been converted to A^-. Therefore, at one half the equivalence point, one half of the HA will have been converted to A^-. So at one half equivalence point, $[HA] = [A^-]$, and the pH at this point will be equal to the pK_a of the acid.



A polyprotic acid is an acid that has more than one acidic hydrogen. Consider the generic acid, H_2A. It will have two K_a values:

$H_2A + H_2O \longrightarrow H_3O^+ + HA^-$ $\quad K_{a1} = [H_3O^+][HA^-]/[H_2A]$

$HA^- + H_2O \longrightarrow H_3O^+ + A^{2-}$ $\quad K_{a2} = [H_3O^+][A^{2-}]/[HA^-]$

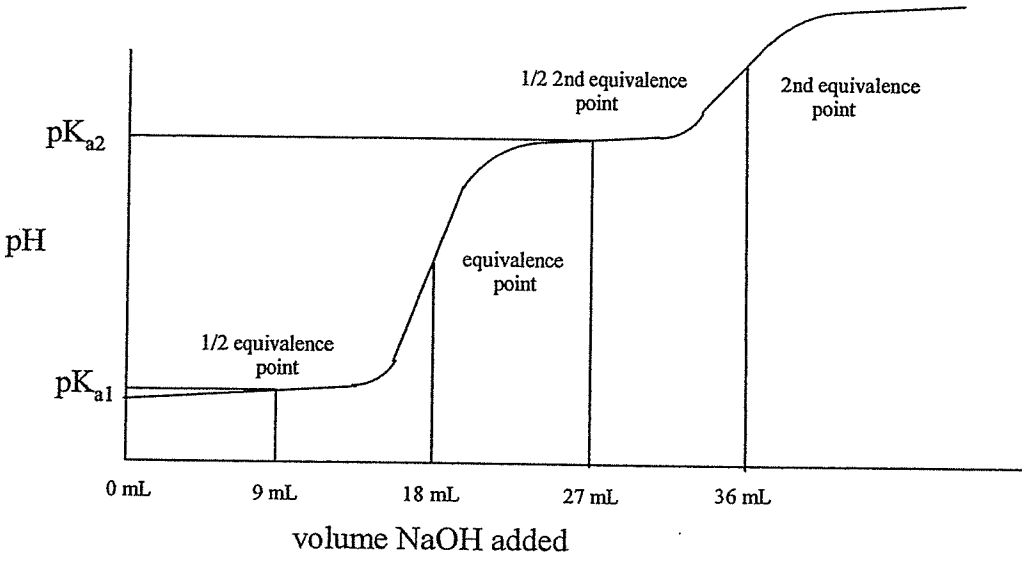
K_{a2} is always much smaller than K_{a1}.

The titration reactions of a polyprotic acid would be:

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

$HA^- + NaOH \longrightarrow H_2O + A^{2-}$

And the titration curve would look something like:



Procedure:

1. Add 25.0 mL of the unknown acid to a 150 mL beaker.

2. Fill the buret with the NaOH solution.

3. Measure the pH of the acid solution. Add 0.5 mL of the base, mix the solution and measure the pH of the acid solution. Repeat the 0.5 mL addition and pH measurement until a minimum of 35 mL of the base has been added.

4. Determine the identity of the unknown acid.

Data:

1. Concentration of the NaOH _____

2. Volume of acid used 25 mL

3. Record data on table
   See next page

Data Table:

Volume Base Added	pH

Volume Base Added	pH

Results:

1. Plot volume of base versus pH.
2. Determine pK_{a1} from graph. 2.14
3. Determine pK_{a2} from graph. 7.21
4. Calculated value of K_{a1}. 7.24×10^{-3}
5. Calculated value of K_{a2}. 6.17×10^{-3}
6. Using the attached list of polyprotic acids, determine the identity of the unknown acid. phosphoric acid

Name of Acid	K_{a1}	K_{a2}
Acetic acid	1.8×10^{-5}	
Boric acid	7.3×10^{-10}	1.8×10^{-13}
Itaconic acid	1.4×10^{-4}	3.6×10^{-6}
Maleic acid	1.5×10^{-2}	8.5×10^{-7}
Malonic acid	1.5×10^{-3}	2.0×10^{-6}
Oxalic acid	5.9×10^{-2}	6.5×10^{-5}
Phosphoric acid	7.3×10^{-3}	6.2×10^{-8}
Tartaric acid	1.0×10^{-3}	4.5×10^{-5}
Salicylic acid	1.0×10^{-3}	4.0×10^{-14}
Ascorbic acid	7.9×10^{-5}	1.6×10^{-12}
D/L Aspartic acid	1.4×10^{-4}	1.5×10^{-10}