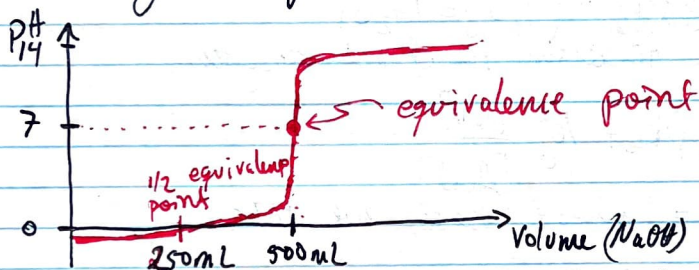## Titration Lab Notes

lets consider a solution of fairly concentrated $HCl_{(aq)}$ acid. Say 5M HCl in 100mL. Assuming full dissociation in water, $[H^+] = [HCl]_i = 5M$. We then know the pH is

$$pH = -\log_{10}[H^+] = -\log_{10}[5] = -0.698$$

Now, when we add NaOH (1M concentration) how does this change the pH?

We know we need 500 mL of the 1M NaOH to fully quench the HCl $\Rightarrow$ pH = 7 at 500mL added.

What we should note is that when we are relatively far from 500mL, the pH won't really change all that much. So at the beginning, it starts out slow. Similarly, after all of the HCl is quenched, the pH will saturate at 14 since we only have $NaOH \rightarrow OH^- + Na^+$ in solution contributing.

The equivalence point is drawn on the graph. It's the point where all acid is consumed. The ½ equivalence point is when ½ acid is consumed. This should typically be ½ volume at the equivalence point.

Note: Suppose we didn't know the concentration of HCl we had. Using the 1st equivalence point we can determine that 500 mL of 1M NaOH was required to neutralize all the HCl. Hence we had

$$(500mL)(1M) = 0.5 \text{ moles } HCl.$$

Knowing we had 100mL of acid to begin with, we can determine that we had a 5M solution?

Hence the equivalence point (use 1st equivalence point for diprotic or triprotic acids) can help identify the concentration.

Lets examine the half-equivalence point a bit more. At this point, we had 250 mL of NaOH. So we know only ½ of the acid is in solution, and ½ of the conjugate base in solution. That is,

$$[H_3O^+] = [H_2O]$$
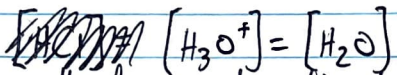
Using the Henderson Hasselback equation,

$$pH = pK_a + \log \frac{[CB]}{[Acid]}$$

where CB = conjugate base, we note

$$\frac{[CB]}{[Acid]} = 1$$

Hence $\log \frac{[CB]}{[Acid]} = 0.8$, pH = pK_a at the ½ equivalence point! Note, that we can also determine these points by means of rudimentary calculus.

Observe that an equivalence point is when the slope of the tangent line is a local maximum (approaches $\pm\infty$). Similarly, midpoints / ½ equivalence points occur when the 2nd derivative is 0. Why?

$f(x)$
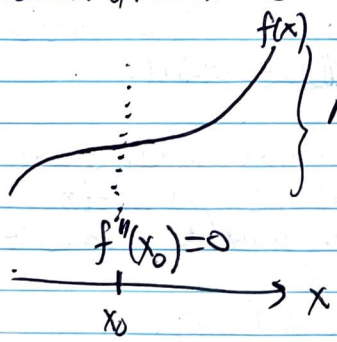
Note a change in curvature from concave down to concave up occurs when 2nd derivative is 0. This is precisely our midpoint. They should also be the minimum points of the first derivative plot.

$f''(x_0) = 0$

x_0

Now say we have a diprotic acid. The titration curve, as well as 1st derivative plot looks like:

pH ↑

B

← 2nd equivalence point

← 1st equivalence point

A

volume →
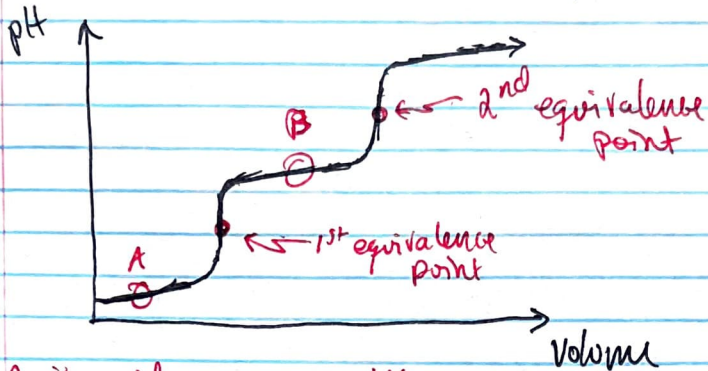
A is midpoint 1, or 1st ½ equivalence
B is midpoint 2, or 2nd ½ equivalence.

A will give pk_{a_1}, B will give pk_{a_2}

$\frac{dpH}{dV}$ ↑

a   b   c   d   V
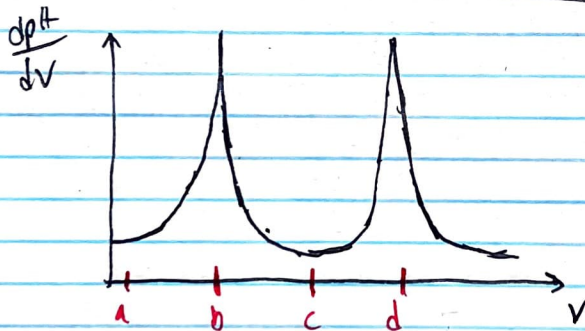
a : c are the ½ equivalence points.

b : d are the equivalence points.