

First Derivative Plots!

It can be fairly difficult to find the endpoint from a standard sigmoidal pH plot - where exactly is the point of steepest slope? To make life easier, we can calculate derivatives, 1st derivative: $\Delta\text{pH}/\Delta V$, or $d\text{pH}/dV$ and the second derivative: $\Delta(\Delta\text{pH}/\Delta V)/\Delta V$ or $d^2\text{pH}/dV^2$. In this class we want to see the first derivative only.

First derivative: How does pH change with volume? Clearly, pH does not change much with volume at the beginning. Only near the endpoint does pH rapidly change, and in fact quickly goes up then more slowly so the derivative plot will show a peak where the top of the peak is the most rapid pH change with volume or the steepest part of the sigmoidal plot. To calculate, simply find the difference between two sequential pH values and divide by the difference between their respective volumes. This is shown in Tables 1a and b. Note that a first derivative volume is shown. The derivative is actually for a volume half way in between the two volumes making the difference in the denominator! The first derivative plot is shown using (hot pink) squares in figure 1. In plotting with excel, I looked up the data definition (shows in formula line when points are highlighted) and changed the x axis to the first derivative even if it is shown on the same axis as the original sigmoidal plot (figure 3).

Table 1a: First derivative values

Table 1b: How to calculate them using Excel

	A	B	C	D		A	B	C	D
	mL	pH	mL ^{1st}	dpH/dV		mL	pH	mL ^{1st}	dpH/dV
42	19.00	2.76	18.75	0.10		19.00	2.76	AVERAGE(B41:B42)	(B42-B41)/(A42-A41)
43	19.50	2.81	19.25	0.11		19.50	2.81	AVERAGE(B42:B43)	(B43-B42)/(A43-A42)
44	20.00	2.87	19.75	0.11		20.00	2.87	AVERAGE(B43:B44)	(B44-B43)/(A44-A43)
45	20.50	2.93	20.25	0.12		20.50	2.93	AVERAGE(B44:B45)	(B45-B44)/(A45-A44)

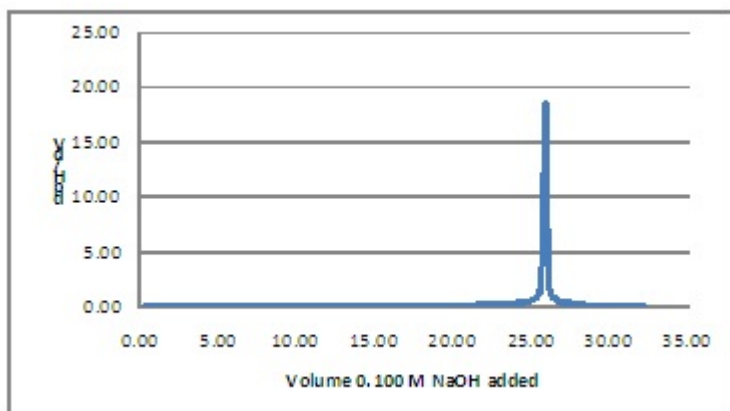


Figure 1: The First derivative plot. The highest point is the endpoint volume.

On the next sheet is a combined plot showing both graphs on a common plot. To prevent one plot from being squished, it is often necessary to use a secondary y-axis. In the latest Excel, click on the data points, right click (sorry MacPeople) and use 'Format data series' to open the menu for picking a secondary axis. You can then battle Excel to put on a label ("Layout", "Axis Titles", "secondary vertical axis").

Bon Chance!

Figure 1: Titration of a strong acid (HCl) with a strong base

