Finding the Equivalence Point on a pH Titration Curve

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The equivalence point in an acid-base titration occurs when a stoichiometrically equivalent amount of titrant has been added to the analyte. It is possible to monitor the pH changes during the titration to determine the equivalence point. When pH is plotted vs. the volume of base added, a titration curve is generated. Figure 1 is a titration curve for the titration of acetic acid with sodium hydroxide (the data are included here as a sidebar). The initial pH is less than 7 and is indicative of the hydrogen ions present in solution resulting from partial dissociation of the acid. As base is added, all of the OH^- added reacts with the H^+ from the acid and more of the weak acid will dissociate. The pH begins to increase slowly because there is less and less H^+ in solution. As the equivalence point is approached, small additions of base cause larger and larger changes in the pH; in the region of the equivalence point, the titration curve appears almost vertical. Beyond the equivalence point, pH is determined by the concentration of excess base present.

mL NaOH	pH
0.00	2.51
1.59	3.35
2.26	3.56
3.58	3.75
4.52	3.99
4.98	4.01
5.25	4.12
6.52	4.32
7.84	4.45
9.56	4.58
10.22	4.76
11.24	4.82
12.18	4.91
13.62	5.08
14.52	5.13
15.08	5.24
15.98	5.38
16.20	5.43
18.34	5.59
19.26	5.85
19.64	6.01
20.21	6.50
20.36	6.80
20.54	7.53
20.70	9.98
20.81	10.30
20.93	10.50
21.03	10.61
21.21	10.72
21.34	10.88
21.47	10.93
21.76	11.02
22.29	11.18
23.64	11.22
24.45	11.34
27.23	11.54
29.45	11.59
36.80	11.61

A Graphical Method to find the Equivalence Point

The equivalence point can be determined from the pH titration curve (figure 2). First, two lines are drawn tangent to the flat portions of the curve (lines A and B). These lines are generally not parallel. Next, perpendicular lines are drawn to these first two tangent lines (lines C). A line perpendicular to the upper tangent is drawn to the lower tangent and a line perpendicular to the lower tangent line is drawn to the upper line. Again, these lines are not necessarily parallel. The midpoints on the perpendiculars are found and connected by a line (D). The point where the bisecting line (D) crosses the titration curve is the equivalence point. The equivalence point volume is found by dropping a perpendicular line (E) from the intersection of the titration curve and line D to the *x*-axis. Here the equivalence point volume (20.6 mL) is read from the graph. As you can see from figure 2, a computer generated graph will generally only allow you to estimate the volume to the nearest tenth of a milliliter, even though the data are precise to two decimal places. Since the answer must have the same precision as the data, this method may require use of a hand drawn graph with greater resolution of the axes.

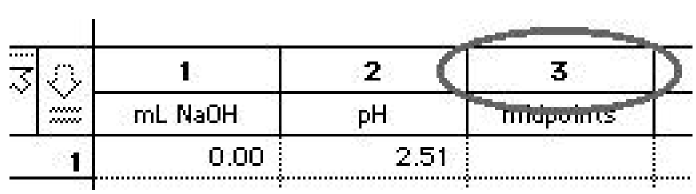
Using the First Derivative of the Data to find the Equivalence Point

Another method for finding the equivalence point involves using the first derivative of the data (a separate handout discusses how to find the derivative of experimental data). The equivalence point occurs when the slope of the titration curve is at a maximum (refer to figure 1). While it may be possible to find that point using just the titration curve, it is much easier to read the point of maximum slope from a plot of the first derivative of the data. Various computer programs, such as *Excel* or the Macintosh program, *Cricket Graph*, may be used for this purpose. Instructions here will assume that you are using *Cricket Graph*, but the strategy is the same no matter what program you use. You will find the slope of each line segment that joins two adjacent points on the titration curve and plot those numbers versus the midpoints (in the *x*-direction) of those line segments.

First find the midpoint between each two adjacent points in the mL NaOH titration data. *Cricket Graph* has a function, NDIF, that returns the difference between a given value and the value before it. If, for each volume value, you subtract from it *half* of the value returned by NDIF, you will have computed the midpoints. Double-click in the box at the top of column 3 and type (followed by return)

=C1 – NDIF(C1,1)/2

Cricket Graph will fill in the values in column 3.



The screen should now look like the illustration at the right. Note that the first box in column 3 is empty; this is as it should be.

C3 =(C1 - (NDIF(C1 , 1) / 2))

	1	2	3
	mL NaOH	pH	midpoints
1	0.00	2.51	
2	1.59	3.35	0.795
3	2.26	3.56	1.925

The next step is to calculate the slope. For each two successive points, you need to calculate the change in pH and divide it by the change in volume. Double click in the box at the top of column 4 and type

=NDIF(C2,1)/NDIF(C1,1)

Once again, Cricket Graph will fill in the values in column 4, leaving the first box empty. Just to make it easier to read the numbers, you will probably want to change the numeric format of the values in the fourth column.

Inspection of the slopes indicates that the maximum slope (15.31) corresponds to a titration volume of 20.62 mL of NaOH added. This information is also shown graphically in figure 3, where the first derivative of the data is superimposed over the titration curve itself.

23	20.36	6.80	20.285	2.0000
24	20.54	7.53	20.45	4.0556
25	20.70	9.98	20.62	15.3125
26	20.81	10.30	20.755	2.9091
27	20.93	10.50	20.87	1.6667

Reference

1. Kildahl, N.; Varco-Shea, T.; *Explorations in Chemistry*, John Wiley & Sons: New York, 1996.