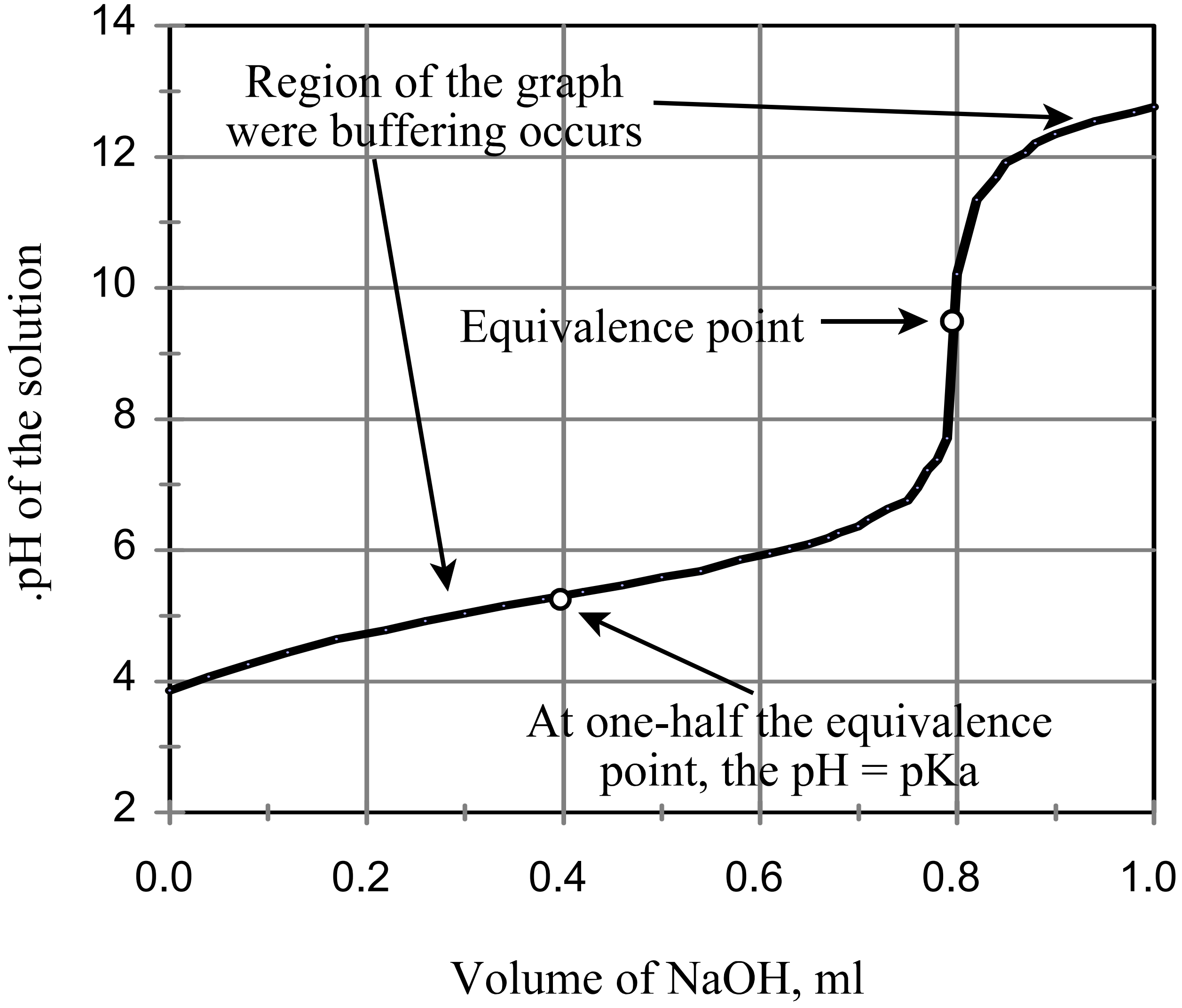
A typical pH titration of a weak monoprotic acid vs a strong base



Equivalence Point - At the equivalence point, the number of moles of aqueous hydrogen ion, $H^+(aq)$, which have been neutralized by exactly the same number of moles of aqueous hydroxide ion, OH^-.

The pH of the solution at the equivalence point equals the pH of the conjugate base solution. For example, if 50 ml of 0.1 M NaOH is neutralized by 50 ml of 0.1 M acetic acid, the result would be 100 ml of 0.05 M sodium acetate solution. The pH of 0.05 M sodium acetate is approximately 8.7.

$$\underset{\text{OAc}^-(aq)}{0.05-x} \quad + \quad H_2O(\ell) \quad \rightleftarrows \quad \underset{\text{HOAc}(aq)}{x} \quad + \quad \underset{\text{OH}^-(aq)}{x}$$

$$K_a = \frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]} = \frac{(x)(x)}{0.05\text{-}x} = 5.6 \text{ x } 10^{-10}$$

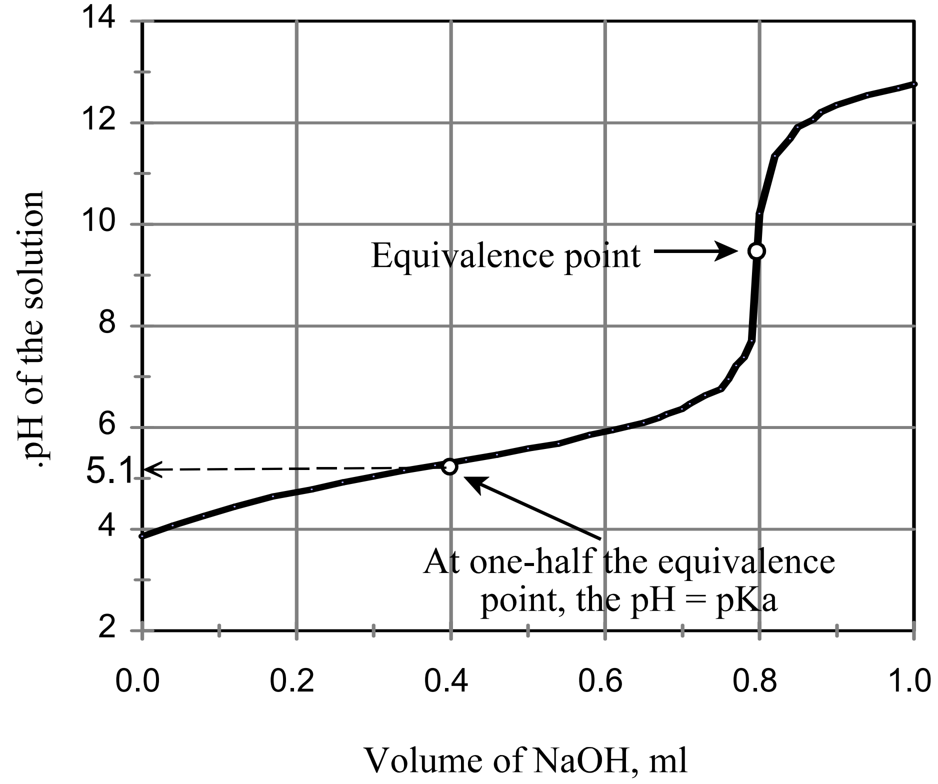
$$x^2 = 5.6 \text{ x } 10^{-10}(0.05 - x) = 2.8 \text{ x } 10^{-11} - 5.6 \text{ x } 10^{-10}x$$

$$x = [\text{OH}^-] = 5.3 \text{ x } 10^{-6} \text{ M}, \quad \text{pH} = 14 - \log(5.3 \text{ x } 10^{-6}) = 8.7$$

One-Half the Equivalence Point - At one-half the equivalence point, exactly one-half of the acid in the solution has been neutralized giving a solution with an equal concentration of both the acid and its conjugate base. Since the concentration of each of the materials is the same, then the pH of this solution equals the pK_a of the acid as predicted by the Henderson-Hasselbach equation:

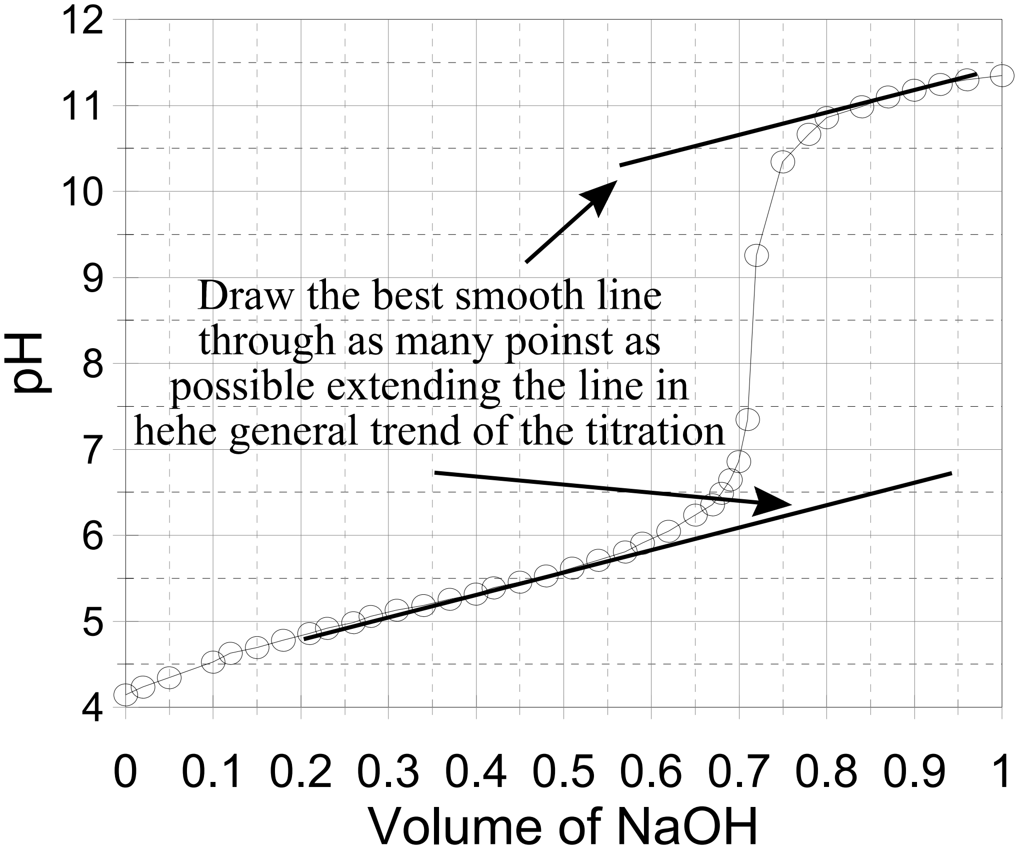
$$pH = pK_a + \log \frac{[Base^-]}{[Acid]}$$

Given this information, the pK_a of an acid may be determined from a pH titration.

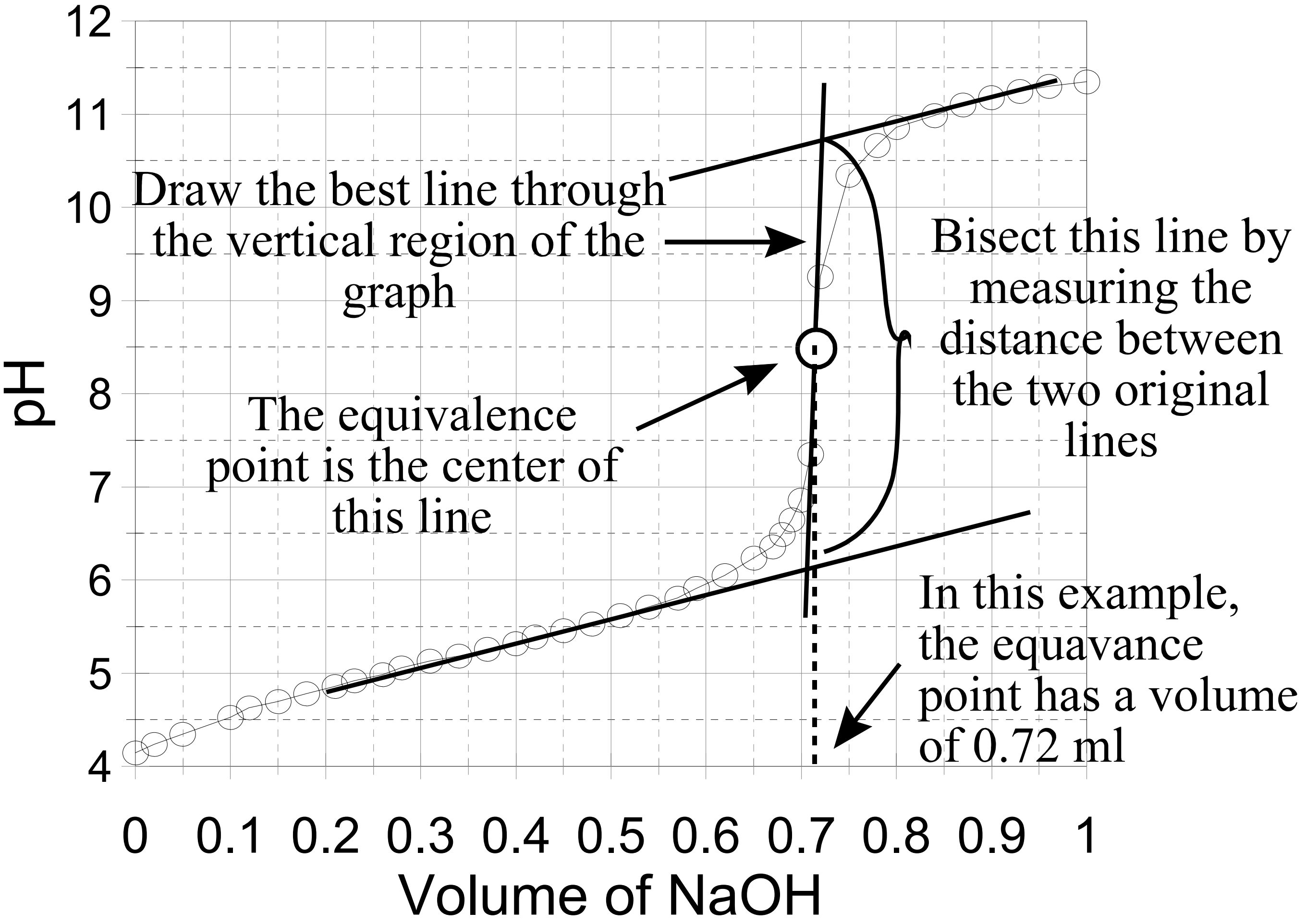


The Determination of the Equivalence Point and pKa Graphically

Step 1. Draw the best straight line through both linear regions of the graph where buffering occurs. The best line represents the general direction of the data, includes as many point as possible, and has as many points above the line as below it. Extend this line beyond the data points so that it may be used in the next step, determining the equivalence point.



Step 2. Draw a line through the portion of the graph with the greatest slope. Measure the length of this line between the two lines drawn in Step #1, and find its center. The center of this line is approximately the equivalence point.



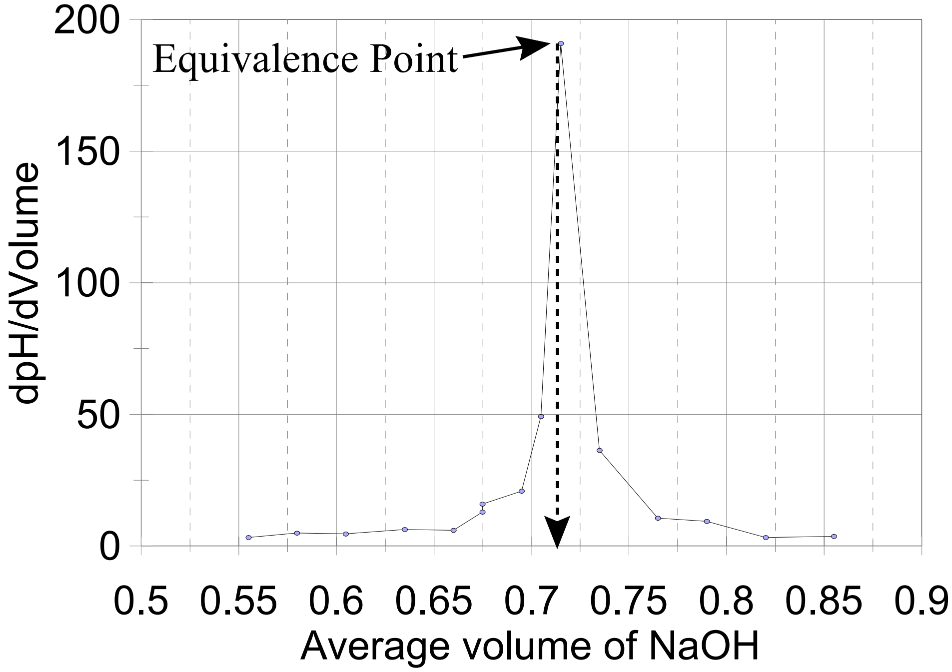
Drop a line perpendicular to the x-axis at this point to determine the volume of titrant added to reach the equivalence point. Once this value is known, the concentration of a monoprotic acid may be determined from the relationship:

$$V_{acid} \text{ x } M_{acid} = V_{base} \text{ x } M_{base}$$

<u>Step 3.</u> Once the equivalence point has been determined, the pK_a of the acid can be obtained. At a volume of one-half the equivalence point volume, the pH of the solution equals the pK_a of the acid. In the adjacent example, the equivalence point volume is 0.72 ml giving a value of 0.36 ml at one-half the equivalence point. The pH of the solution when 0.36 ml of base has been added to the solution is 5.3. Consequently, the pK_a of this acid would be 5.3

Determining the Equivalence Point of a Titration by Use of the First Derivative Plot

If the simple pH titration graph studied earlier does not provide the equivalence point with certainty, then a first derivative plot of the data in the region of the equivalence point may be utilized. The equivalence point of a titration occurs precisely at the inflection point that separates the concave portion of the graph from the convex portion of the graph. The slope reaches a maximum at this point. By plotting the change in the slope ( ) pH/) Volume) vs the average volume of titrant, the equivalence point can be readily determined.



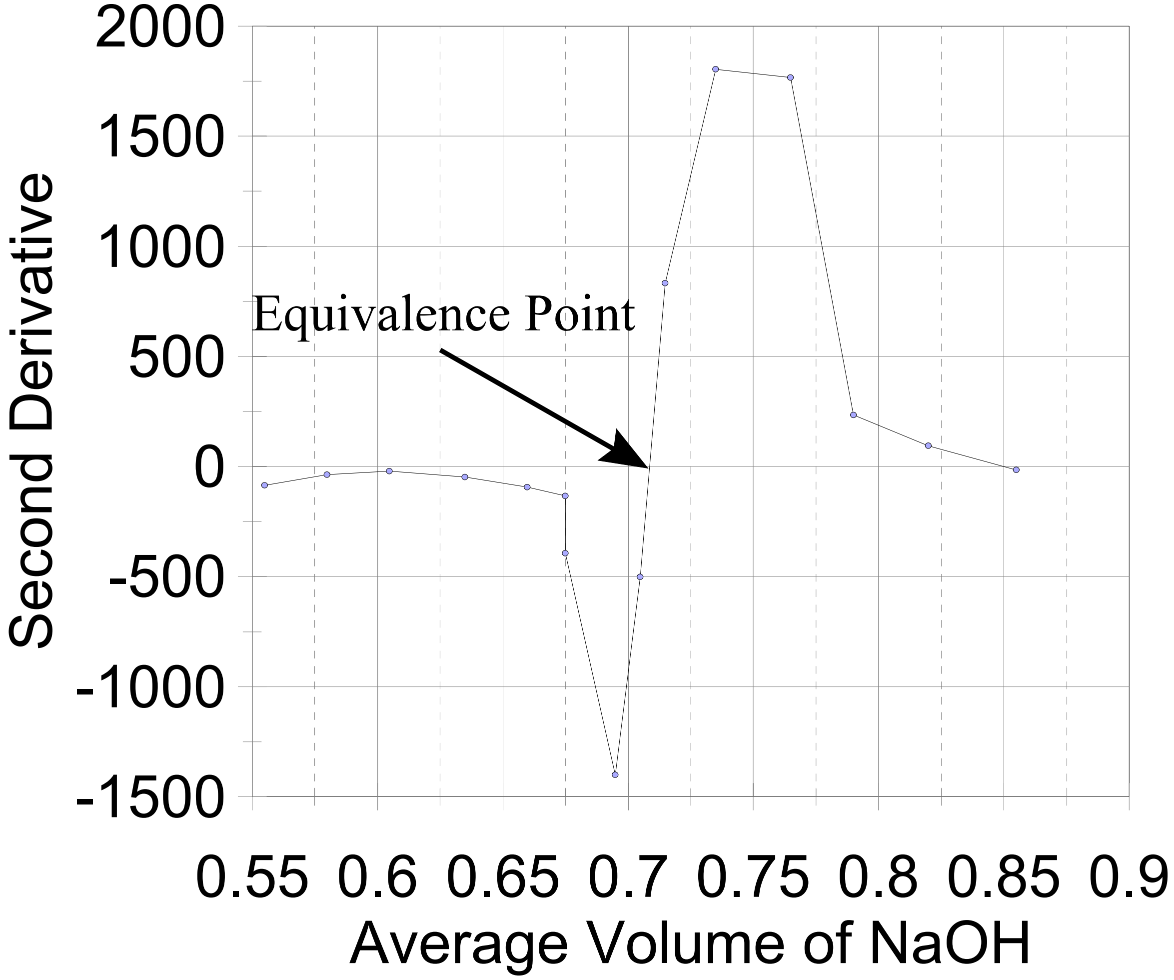
To prepare the first derivative graph, calculate the slope ( ) pH/) Volume) and average volume of titrant within ±0.15 ml of the predicted equivalence point. Note the sample calculations in the table below.

Volume of NaOH	pH	$\frac{\Delta pH}{\Delta Volume}$	Average Volume
0.68 ml	6.49		
		$\frac{6.86-6.49}{0.72-0.68}=18.5$	$\frac{0.68+0.72}{2}=0.69\text{ ml}$
0.70 ml	6.86		
		$\frac{9.26-6.86}{0.72-0.70}=120$	$\frac{0.70+0.72}{2}=0.71\text{ ml}$
0.72 ml	9.26		

After all the calculations are made, the slope (the change in the pH over the change in the volume of NaOH) is then plotted against the average volume of titrant (NaOH) for each point calculated. The equivalence point for the titration would occur where the change in the pH over the change in the volume is a maximum. Note the first derivative plot above.

Determining the Equivalence Point of a Titration by Use of the Second Derivative Plot

If the first derivative graph does not give a satisfactory value for the equivalence point, a second derivative of the graph may be prepared.



In the second derivative graph, the change in the slope from the first derivative data table ( ) pH/) volume) is plotted against the change in the average volume. The equivalence point occurs where the change in the slope is zero. Observe the adjacent second derivative plot.

Average Volume	$\frac{\Delta pH}{\Delta Volume}$	$\frac{\Delta(\Delta pH)}{\Delta(\Delta Volume)}$	Average of the Average Volume of NaOH Reacted
0.69 ml	18.5		
		$\frac{120-18.5}{0.71-0.69}=5075$	$\frac{0.69+0.71}{2}=0.70$
0.71 ml	120		

Determining the pK_a of a Weak Acid Mathematically

Another method which may be used to determine the pK_a of a weak acid is to calculate the pHa from a variation in the Henderson-Hasselbach equation:

$$pK_a = pH_{dp} - \log\left(\frac{V_{dp}}{V_{ep} - V_{dp}}\right)$$

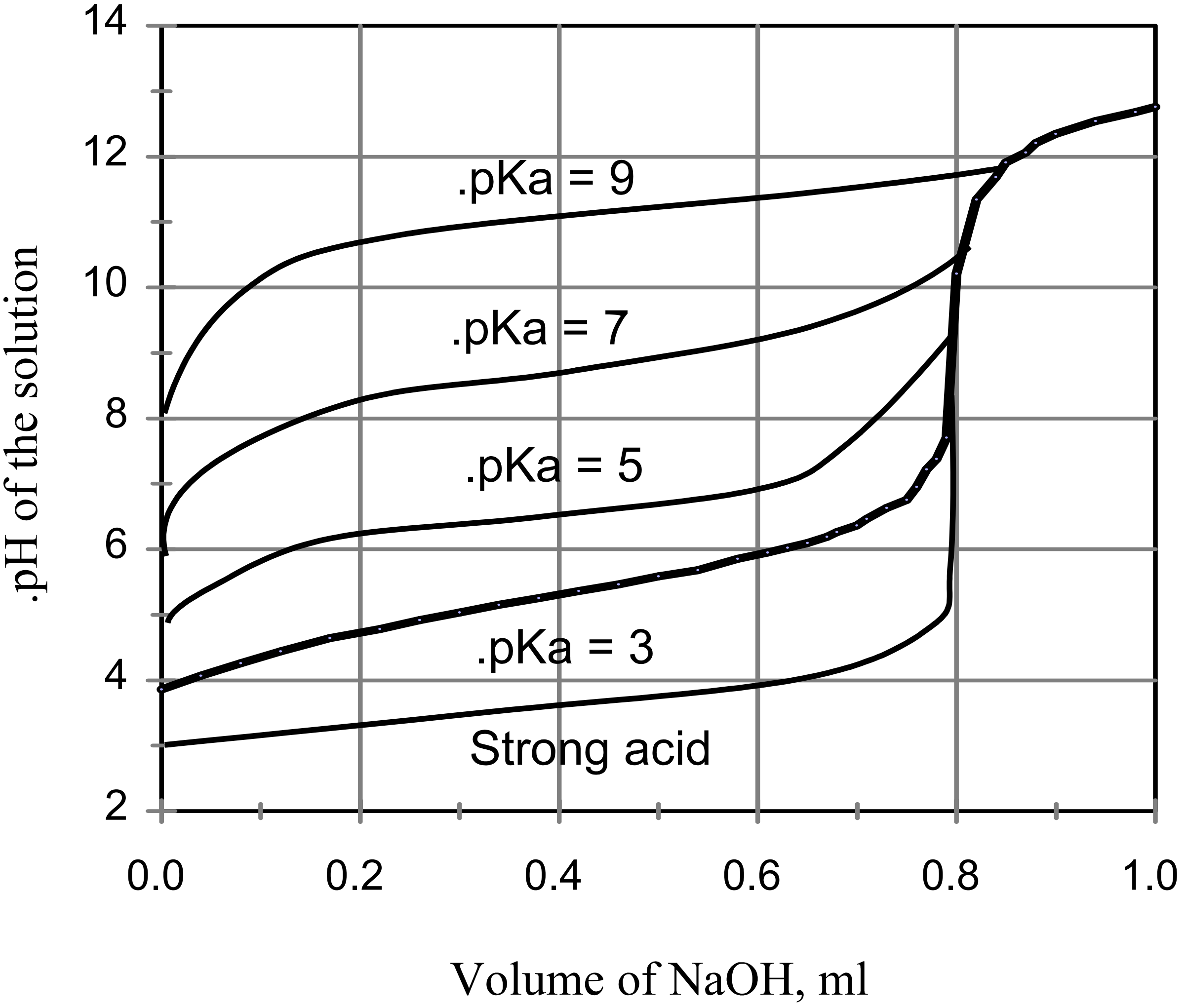
where V_{ep} is the volume of the titrant needed to arrive at the equivalence point and V_{dp} represents the total volume of the titrant added at the data point.

Choose several data points in the linear portion of the pH titration near one-half the equivalence point, calculate the pK_a at each point, and average these values. The data in the table above is taken from the pH titration studied earlier which has an equivalence point at 0.72 ml. Using the first data point in the table above, the pK_a calculates to be 5.25 with an average value is 5.24.

$$pK_a = 5.13 - \log\left(\frac{0.31}{0.72-0.31}\right) = 5.25$$

Volume	pH	pKa
0.31 ml	5.13	5.25
0.34 ml	5.19	5.24
0.37 ml	5.26	5.24
0.40 ml	5.32	5.22
0.42 ml	5.39	5.24

The Influence of the Strength of the Acid on the Shape of the Titration Curve



Selecting the Proper Indicator for a pH Titration