

Titration Curve of a Weak Monoprotic Acid

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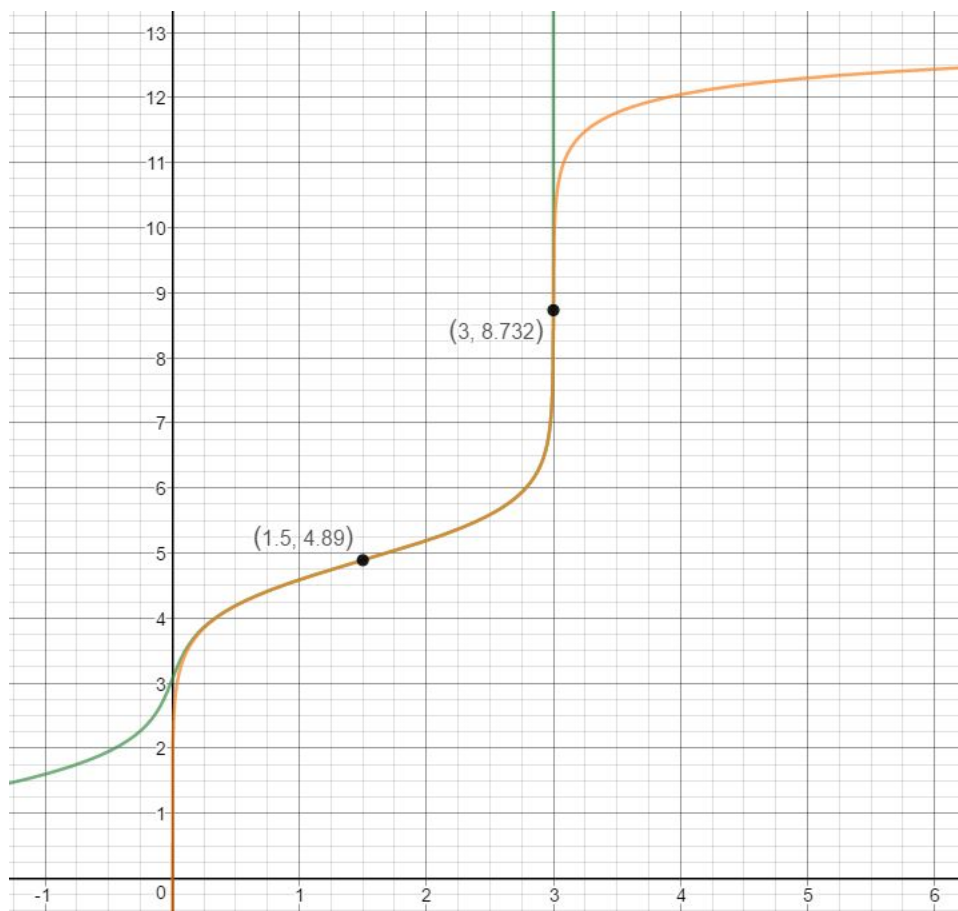
1 An Example

5mL of weak acid HA ($pK_a = 4.89$) with concentration of 0.06M is titrated against 0.1M KOH.

We want to plot the titration curve, against the amount of titrant added x ml.

The result is available on Desmos, an online graphing calculator:

<https://www.desmos.com/calculator/znyxkzgaxw>



1.1 Before Equivalence Point

With x amount of titrant KOH, the total volume of the solution is $x + 5$. The initial condition is defined to have all the OH^- added to react with HA to form A^- : $\text{OH}^- + \text{HA} \longrightarrow \text{A}^- + \text{H}_2\text{O}$

The initial number of moles of HA is $(3 - x) \times 0.1\text{mol}$

Hence, the initial concentration of HA is $\left(\frac{3-x}{x+5}\right) \times 0.1\text{M}$

The initial number of moles of A^- is $x \times 0.1\text{mol}$

Hence, the initial concentration of A^- is $\left(\frac{x}{x+5}\right) \times 0.1\text{M}$

We thus construct the following Initial-Change-Equilibrium table:

	[HA]	[H ⁺]	[A ⁻]
Initial	$0.1 \frac{3-x}{x+5}$	0	$0.1 \frac{x}{x+5}$
Change	$-m$	$+m$	$+m$
Eqbm	$0.1 \frac{3-x}{x+5} - m$	m	$0.1 \frac{x}{x+5} + m$

At equilibrium, the concentrations [HA], [H⁺], [A⁻] satisfy the K_a value.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{m \left(0.1 \frac{x}{x+5} + m\right)}{0.1 \frac{3-x}{x+5} - m}$$

$$0 = m^2 + \left(0.1 \frac{x}{x+5} + K_a\right) m - \left(0.1 K_a \frac{3-x}{x+5}\right)$$

We can solve for m with the quadratic equation:

$$[\text{H}^+] = m = \frac{-\left(0.1 \frac{x}{x+5} + K_a\right) + \sqrt{\left(0.1 \frac{x}{x+5} + K_a\right)^2 + 4 \left(0.1 K_a \frac{3-x}{x+5}\right)}}{2}$$

There will be a positive root. The negative root is rejected because the concentration cannot be negative. We are now able to plot the titration curve:

$$\text{pH} = -\log[\text{H}^+] = -\log \left(\frac{-\left(0.1 \frac{x}{x+5} + K_a\right) + \sqrt{\left(0.1 \frac{x}{x+5} + K_a\right)^2 + 4 \left(0.1 K_a \frac{3-x}{x+5}\right)}}{2} \right)$$

The curve is only valid for $x \leq 3$. It is not valid for $x > 3$ because there will be remaining OH^- , which cannot be reflected in the Initial-Change-Equilibrium table. A separate set of calculations needs to be made.

1.2 At Equivalence Point

At the equivalence point, all HA is neutralised by KOH. The solution can be thought as adding KA salt into pure water. The Initial-Change-Equilibrium table can be constructed as follows:

	[HA]	[OH ⁻]	[A ⁻]
Initial	0	0	$0.1 \frac{3}{5+3}$
Change	+ m	+ m	- m
Eqbm	m	m	$0.1 \frac{3}{5+3} - m$

At equilibrium, the concentrations [HA], [OH⁻], [A⁻] satisfy the K_b value.

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{m^2}{0.1 \frac{3}{5+3} - m}$$

$$0 = m^2 + K_b m - 0.1 K_b \frac{3}{5+3}$$

We can solve for m with the quadratic equation:

$$[\text{OH}^-] = m = \frac{-K_b + \sqrt{K_b^2 + 4 \left(0.1 K_b \frac{3}{5+3} \right)}}{2}$$

Once again, the positive root is taken so that the concentration of [OH⁻] is not negative. We can thus calculate the pH of the equivalence point:

$$pH = pK_w - pOH = 14.00 - 5.33 = 8.67$$

1.3 After Equivalence Point

At the equivalence point, all of HA is already neutralised by KOH. The initial state solution can be thought as adding KA salt into pure water, and then adding unreacted KOH. The Initial-Change-Equilibrium table can be constructed as follows:

	[HA]	[OH ⁻]	[A ⁻]
Initial	0	$0.1 \frac{x+3}{x+5}$	$0.1 \frac{3}{x+5}$
Change	+m	+m	-m
Eqbm	m	$0.1 \frac{x+3}{x+5} + m$	$0.1 \frac{3}{x+5} - m$

At equilibrium, the concentrations [HA], [OH⁻], [A⁻] satisfy the K_b value.

$$K_b = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = \frac{m \left(0.1 \frac{x-3}{x+5} + m \right)}{0.1 \frac{3}{x+5} - m}$$

$$0 = m^2 + \left(0.1 \frac{x-3}{x+5} + K_b \right) m - \left(0.1 K_b \frac{3}{x+5} \right)$$

We can solve for m with the quadratic equation:

$$m = \frac{- \left(0.1 \frac{x-3}{x+5} + K_b \right) + \sqrt{\left(0.1 \frac{x-3}{x+5} + K_b \right)^2 + 4 \left(0.1 K_b \frac{3}{x+5} \right)}}{2}$$

We can thus calculate the pH and plot the remaining titration curve:

$$\begin{aligned} pH &= pK_w - pOH = 14.00 + \log \left(m + \left(0.1 \frac{x-3}{x+5} \right) \right) \\ &= 14.00 + \log \left(\frac{- \left(0.1 \frac{x-3}{x+5} + K_b \right) + \sqrt{\left(0.1 \frac{x-3}{x+5} + K_b \right)^2 + 4 \left(0.1 K_b \frac{3}{x+5} \right)}}{2} + \left(0.1 \frac{x-3}{x+5} \right) \right) \end{aligned}$$