Titration of a Monoprotic Weak Acid with the Strong Base, NaOH

First, we drive the "exact"expression for $[H^+]$ in the titration of V_a mL of a monoprotic acid, HA, at an initial concentration C_a, with acid ionization constant K_a. as we add V_b mL of an NaOH solution of concentration C_b. [The analysis does not depend on the precise nature of the strong base.]

The unknown concentrations are: $[H^+]$, $[OH^-]$, $[HA]$, $[A^-]$.
The relations between them and the known volumes and concentrations are:

1. K_w: $\qquad$ $[H^+] [OH^-] = K_w$

2. K_a: $\qquad \dfrac{[H^+]\ [A^-]}{[HA]} = K_a$

3. Charge Conservation: $\quad [H^+] + [Na^+] = [A^-] + [OH^-]$

4. Mass Conservation: $[HA] + [A^-] = C_aV_a/ (V_a + V_b)$ where C_a and V_a are the initial values of the concentration and volume of

$\qquad$ HA and V_b is the volume of base of concentration C_b added to the solution

5. Then, $\qquad\qquad [Na^+] = C_bV_b / (V_a + V_b)$

We would like to write Equation 3. in terms of only one unknown, $[H^+]$, and the known quantities, $K_w, K_a, C_a, V_a, C_b, V_b$

6. Rearrange 1 $\qquad [OH^-] = K_w / [H^+]$

7. Rearranging 4 for $[A^-]$, substituting the value for $[HA]$ from 2: $\quad [A^-] = C_aV_a/(V_a + V_b) - [HA] = C_aV_a/(V_a + V_b) - [H^+][A^-] / K_a$

8. Solve 7 for $[A^-]$ $\quad [A^-] = \{C_aV_a / (V_a + V_b)\} / (1 + [H^+] / K_a)$

9. Substitute 5, 6, and 8 into 3

$[H^+] + \qquad [Na^+] \qquad\qquad = \qquad\qquad [A^-] \qquad\qquad\qquad + \quad [OH^-]$

$[H^+] + \qquad C_bV_b / (V_a + V_b) \qquad = \qquad \{C_aV_a / (V_a + V_b)\} / (1 + [H^+] / K_a) + K_w / [H^+]$

10. Multiply by $[H^+]$ and rearrange as a polynomial equation

$$[H^+]^2 + [H^+]\,C_bV_b / (V_a + V_b) \;-\; [H^+]\,\{C_aV_a / (V_a + V_b)\} / (1 + [H^+] / K_a) \;-\; K_w = 0$$

11. Clear the remaining term with $[H^+]$ in the denominator, and collect powers of $[H^+]$

$$[H^+]^3 + [H^+]^2\,\{K_a + C_bV_b /(V_a + V_b)\} + [H^+]\,K_a\,\{(C_bV_b - C_aV_a)/ (V_a + V_b) - K_w / K_a\} - K_wK_a = 0$$

The solutions to this cubic equation are the values that $[H^+]$ must satisfy for any values of the known quantities.

12. Before any base is added, $V_b = 0$ and the equation reduces to:

$$[H^+]^3 + [H^+]^2\,K_a - [H^+]\,K_a\,\{C_a + K_w / K_a\} - K_wK_a = 0$$

This is the exact solution to the $[H^+]$ of a monoprotic weak acid.

An approximation to this equation is often invoked by arguing that, for most acids, K_wK_a can be neglected compared to zero. This reduces the cubic equation to a quadratic equation, namely:

12a $\qquad\qquad\qquad\qquad [H^+]^2 + [H^+]\,K_a - K_a\,\{C_a + K_w / K_a\} = 0$

Or if $K_w / K_a \ll C_a$, even further to:

12b $\qquad\qquad\qquad\qquad [H^+]^2 + [H^+]\,K_a - C_aK_a = 0$

13. At the The <u>Equivalence Point</u>, the moles of added base are equal to the moles of acid titrated. I.e., $C_aV_a = C_bV_b$ and the value of $[H^+]$ is the solution to:

13. $$[H^+]_{eq}^3 + [H^+]_{eq}^2\ \{K_a + C_a V_a/(V_a + V_b)\} - [H^+]_{eq} K_w - K_wK_a = 0$$

Like above, an approximation to this equation is often invoked by assuming that K_wK_a can be neglected compared to zero.   This again reduces the cubic equation to a quadratic equation, namely:

13a. $$[H^+]_{eq}^2 + [H^+]_{eq}\ \{K_a + C_a V_a/ (V_a + V_b)\} - K_w = 0$$

which can be solved in closed form. This equation is also the solution to $[H^+]$ of a solution of the salt of a strong base and weak acid caused by hydrolysis of the salt. $C_a V_a / (V_a + V_b)$ will be recognized as simply the actual concentration of the salt.

What about the point at which $[HA] = [A^-]$ **?** At that point, $[H^+] = K_a$. Substituting K_a for $[H^+]$ permits us to calculate the volume of added base, V_b for a fixed initial moles of acid of known K_a , namely, C_aV_a and the concentration of the base, C_b.

14. $$K_a^3 + K_a^2 \{ K_a + C_bV_b/(V_a + V_b)\} + K_a K_a \{ (C_bV_b - C_aV_a)/ (V_a + V_b) - K_w / K_a \} - K_wK_a = 0$$

Solving this equation for V_b we get:

15. $$V_b = \frac{V_a(K_aC_a + 2 K_w - 2 K_a^2)}{2 K_aC_b - 2 K_w + 2 K_a^2}$$

which can be rearranged to:

17. $$V_b = \frac{C_aV_a (1 + 2 K_w/K_aC_a - 2 K_a/C_a)}{2C_b (1 - K_w/K_aC_b + K_a/C_b)}$$

But, the quantity C_aV_a/C_b is precisely the volume of base required to reach the equivalence point. So, if the two quantities in parentheses are close to 1, we will have that:

$$V_b \approx V_b^{eq} / 2$$

In the pH titration exercise, we use sodium hydroxide of approximately 0.05 M concentration and adjust the amount of acid used so that we will require about 25 mL of the base to reach the equivalence point to titrate the acid when it is initially dissolved in 40 mL of water. The values of the quantities in Equation 17 are, then, as follows:

$$C_b = 0.05 \text{ M} \qquad V_a = 40 \text{ mL} \qquad C_a = 25 \times 0.05 / 40 \sim 0.03 \text{ M}$$

The end point in such a titration will be at $C_a V_a / C_b \sim 24$ mL of added base. At what volume of base will the pH equal the pK_a of the acid? Substituting the above values into Equation 17 gives:

18. $$V_b = \frac{C_aV_a (1 + 2 K_w/K_aC_a - 2 K_a/C_a)}{2C_b (1 - K_w/K_aC_b + K_a/C_b)} = \frac{12 (1 + 6.7 \times 10^{-13} / K_a - 2 K_a/.03)}{(1 - 2.0 \times 10^{-13} / K_a + K_a/.05)}$$

For the above conditions, the answer depends on the pK_a of the acid as shown in Table 1 below.

pK_a	Volume when [A⁻] = [HA] (from Equation 18)	% Deviation from 12.0 mL
2	3.3	72%
3	11.0	8%
4	11.9	0.8
5	12.0	0
6	12.0	0
7	12.0	0
8	12.0	0

Table 1 Percent Deviation of Half Titration Volume and Calculated Volume at which [A-] = [HA]

19. Should we be concerned with the large deviation between the actual volumes at which the pH is equal to the pK_a and the half titration point when the pK_a is small? Equation 11 reduces to the following at the half titration point ($V_b = C_a V_a / 2 C_b$)

$$[H^+]^3 + [H^+]^2 \{ K_a + C_a /(1 + C_a/2C_b)\} - [H^+] K_a \{ C_a/2 (1 + C_a/2C_b) + K_w / K_a \} - K_w K_a = 0$$

Probably not.   Table 2 shows the pH at the actual half equivalence point of the above titrations (i.e. 12 mL of added base) and the deviations of those values from the actual pK_a of the acid[*].   While the potential percent error in pK_a is 17% at a pK_a of 2, the table of acids provided in this exercise has a disclaimer that the listed pK_as should be viewed as good only to ± 0.5 units.

pK_a	pK_a at Half Titration Point	% Deviation from Actual pK_a
2	2.35	17%
3	3.06	2%
4	4.00	0%
5	5.00	0%
6	6.00	0%
7	7.00	0%
8	8.00	0%

Table 2 Percent Deviation of pK_a at Half Titration Volume and actual pK_a

It is interesting to see how three critical points in the titration curve depend on the pK_a of the acid.   The graph below shows the dependence of the:
   Initial pH
   pH at the half titration point
     pH at the titration point
on pK_a assuming that 40 mL of a 0.03 M solution of the acid is titrated with 0.05 M NaOH. Note for example that the difference in pH between the initial acid solution and the pH at the equivalence point is constant.

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[*] The calculated pK_a values were obtained by solving the cubic equation in paragraph 19

pH Titration - Major Parameters vs pK$_a$
40 mL of 0.03 M Acid Titrated with 0.05 M NaOH
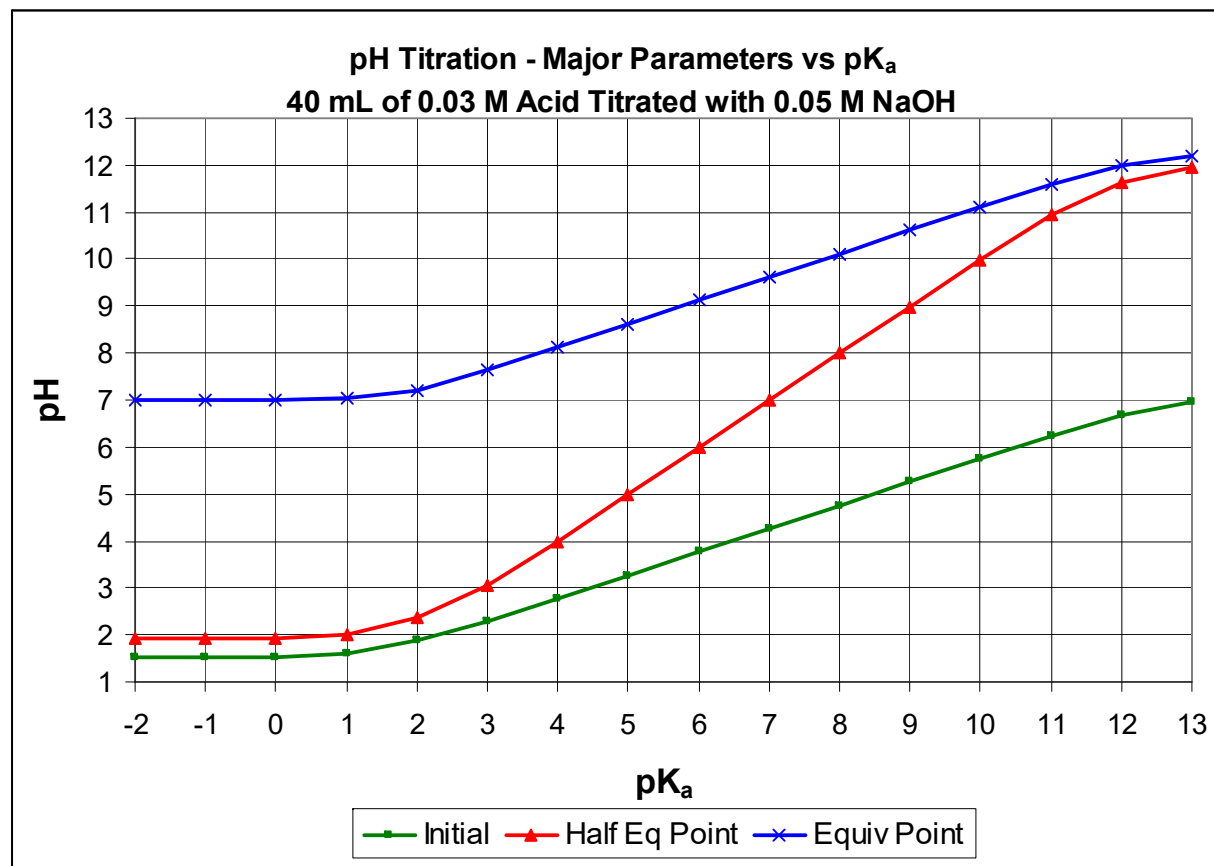
The graphs below shows titration curves for acids with $pK_a = 2$ and $pKa = 7$ with other conditions the typical ones shown above.

Titration of 40 mL of a 0.03 M Acid with pK_a = 2

Titration of 40 mL of 0.03 M Acid with pK_a = 7
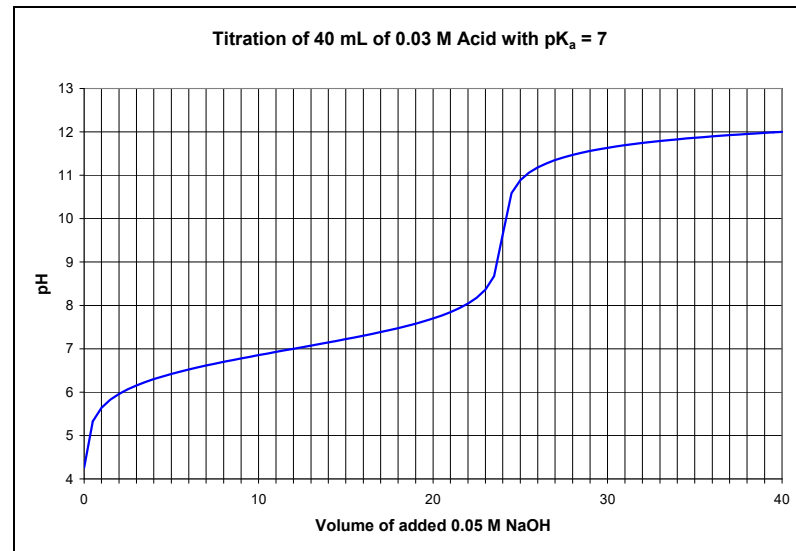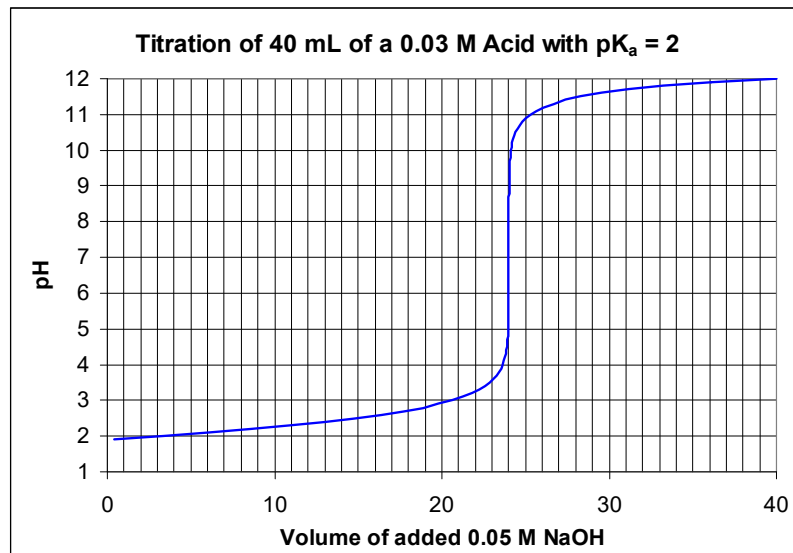
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