

12-1. The equivalence point occurs when the quantity of titrant is exactly the stoichiometric amount needed for complete reaction with analyte. The end point occurs when there is an abrupt change in a physical property, such as pH or indicator color. Ideally, the end point is chosen to occur at the equivalence point.

12-2.

V_a	0	1	5	9	9.9	10	10.1	12
pH	13.00	12.95	12.68	11.96	10.96	7.00	3.04	1.75

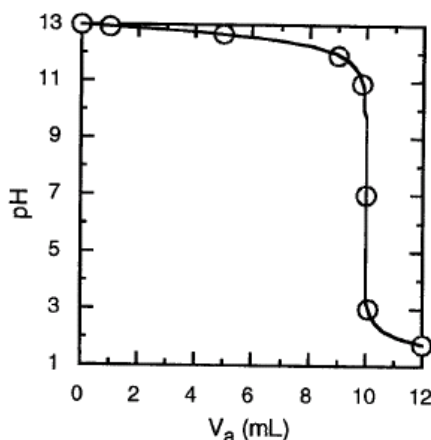
Representative calculations:

0 mL: $\text{pH} = -\log \frac{K_w}{[\text{OH}^-]} = -\log \frac{10^{-14}}{0.100} = 13.00$

1 mL: $[\text{OH}^-] = \frac{9}{10}(0.100) \frac{100}{101} = 0.0891 \text{ M} \Rightarrow \text{pH} = 12.95$

10 mL: $[\text{OH}^-] = [\text{H}^+] = 10^{-7} \text{ M}$

10.1 mL: $[\text{H}^+] = \left(\frac{0.1}{110.1}\right)(1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.04$



12-3. Consider the titration curve near the equivalence point. If we titrate strong acid with strong base, the concentration of H^+ is close to 1% of its initial value when we are 99% of the way to the equivalence point (ie, when $V_b = 0.99V_e$). (This statement would be exactly true if there were no dilution occurring. We will neglect dilution.) If the initial acid concentration were, say, 0.1 M, then $[\text{H}^+] = 1\%$ of 0.1 M = 0.001 M at $V_b = 0.99 V_e$. The pH is $-\log(0.001) = 3$. At 99.9% completion, $[\text{H}^+] = 0.1\%$ of 0.1 M = 0.0001 M and the pH is 4. When the titration is 0.1% past the equivalence point, $[\text{OH}^-] = 0.0001 \text{ M}$ and the pH is $-\log(K_w/0.0001) = 10$. The pH jumps from 4 to 10 in the interval from $V_b = 0.999V_e$ to $1.001V_e$. Even though the concentration of H^+ hardly changes, its logarithm changes rapidly around the equivalence point because $[\text{H}^+]$ decreases by orders of magnitude with tiny additions of OH^- when there is hardly any H^+ present.

12-4. The sketch should look like Figure 12-2. Before base is added, the pH is determined by the acid dissociation reaction of HA. Between the initial point and the equivalence point, each mole of OH⁻ converts an equivalent quantity of HA into A⁻. The resulting buffer containing HA and A⁻ determines the pH. At the equivalence point, all HA has been converted to A⁻. The pH is controlled by the base hydrolysis reaction of A⁻ with H₂O. After the equivalence point, excess OH⁻ is being added to the solution. To a good approximation, the pH is determined just by the concentration of excess OH⁻.

12-5. If the analyte is too weak or too dilute, there is very little change in pH at the equivalence point.

12-6.

V_b	0	1	5	9	9.9	10	10.1	12
pH	3.00	4.05	5.00	5.95	7.00	8.98	10.96	12.25

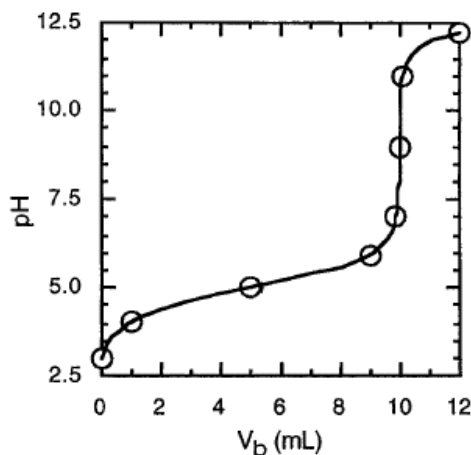
Representative calculations:

$$\begin{array}{l} \underline{0 \text{ mL:}} \quad \text{HA} = \text{H}^+ + \text{A}^- \\ \quad \quad \quad 0.100 - x \quad x \quad x \end{array} \quad \frac{x^2}{0.100 - x} = 10^{-5.00} \Rightarrow x = 9.95 \times 10^{-4} \text{ M} \\ \Rightarrow \text{pH} = 3.00$$

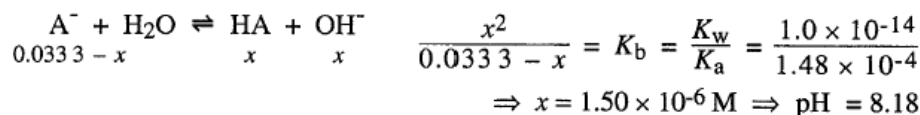
$$\underline{1 \text{ mL:}} \quad \text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]} = 5.00 + \log \frac{1}{9} = 4.05$$

$$\begin{array}{l} \underline{10 \text{ mL:}} \quad \text{A}^- + \text{H}_2\text{O} = \text{HA} + \text{OH}^- \\ \left(\frac{100}{110}\right)(0.100) - x \quad x \quad x \end{array} \quad \frac{x^2}{0.0909 - x} = \frac{K_w}{K_a} \\ \Rightarrow x = 9.53 \times 10^{-6} \\ \Rightarrow [\text{H}^+] = \frac{K_w}{x} \Rightarrow \text{pH} = 8.98$$

$$\underline{10.1 \text{ mL:}} \quad [\text{OH}^-] = \left(\frac{0.1}{110.1}\right)(1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 10.96$$



- 12-8.** The titration reaction is $\text{HA} + \text{OH}^- \rightarrow \text{A}^- + \text{H}_2\text{O}$. A volume of V mL of HA will require $2V$ mL of KOH to reach the equivalence point, because $[\text{HA}] = 0.100 \text{ M}$ and $[\text{KOH}] = 0.0500 \text{ M}$. The formal concentration of A^- at the equivalence point will be $\left(\frac{V}{V+2V}\right)(0.100) = 0.0333 \text{ M}$. The pH is found by writing

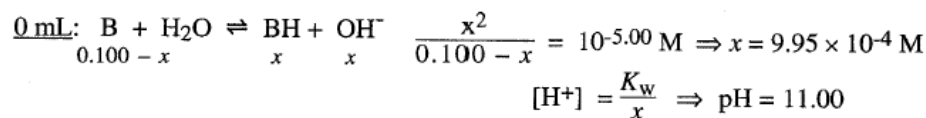


- 12-12.** The sketch should look like Figure 12-9. Before base is added, the pH is determined by the base hydrolysis reaction of B with H_2O . Between the initial point and the equivalence point, each mole of H^+ converts an equivalent quantity of B into BH^+ . The resulting buffer containing B and BH^+ determines the pH. At the equivalence point, all B has been converted to BH^+ . The pH is controlled by the acid dissociation reaction of BH^+ . After the equivalence point, excess H^+ is being added to the solution. To a good approximation, the pH is determined just by the concentration of excess H^+ .

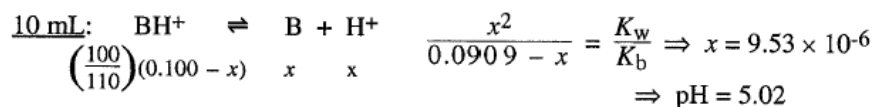
- 12-13.** At the equivalence point, the weak base, B, is converted completely to the conjugate acid, BH^+ , which is necessarily acidic.

- 12-14.**
- | | | | | | | | | |
|-------|-------|------|------|------|------|------|------|------|
| V_a | 0 | 1 | 5 | 9 | 9.9 | 10 | 10.1 | 12 |
| pH | 11.00 | 9.95 | 9.00 | 8.05 | 7.00 | 5.02 | 3.04 | 1.75 |

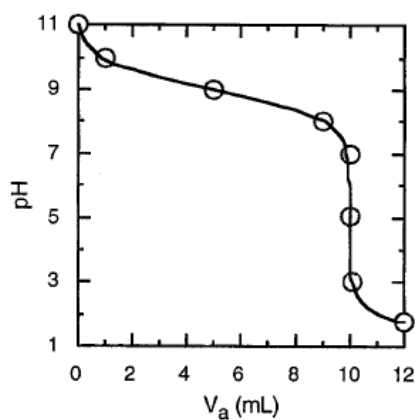
Representative calculations:



$$\text{1 mL: } \text{pH} = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]} = 9.00 + \log \frac{9}{1} = 9.95$$



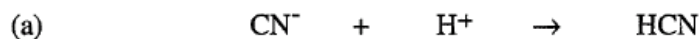
$$\text{10.1 mL: } [\text{H}^+] = \left(\frac{0.1}{110.1}\right)(1.00) = 9.08 \times 10^{-4} \text{ M} \Rightarrow \text{pH} = 3.04$$



12-18. Titration reaction : $\text{CN}^- + \text{H}^+ \rightarrow \text{HCN}$

At the equivalence point, moles of $\text{CN}^- = \text{moles of H}^+$

$$(0.100 \text{ M})(50.00 \text{ mL}) = (0.438 \text{ M})(V_e) \Rightarrow V_e = 11.42 \text{ mL}$$



Initial : 11.42 4.20 —

Final : 7.22 — 4.20

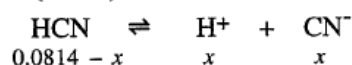
$$\text{pH} = \text{p}K_a + \log \frac{7.22}{4.20} = 9.45$$

(b) 11.82 mL is 0.40 mL past the equivalence point.

$$[\text{H}^+] = \left(\frac{0.40}{61.82} \right) (0.438 \text{ M}) = 2.83 \times 10^{-3} \text{ M} \Rightarrow \text{pH} = 2.55$$

(c) At the equivalence point we have made HCN at a formal concentration of

$$\left(\frac{50.00}{61.42} \right) (0.100) = 0.0814 \text{ M.}$$



$$0.0814 - x$$

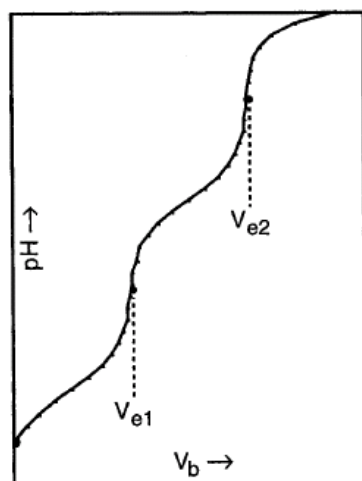
$$x$$

$$x$$

$$\frac{x^2}{0.0814 - x} = K_a \Rightarrow x = 7.1 \times 10^{-6}$$

$$\Rightarrow \text{pH} = 5.15$$

12-19.

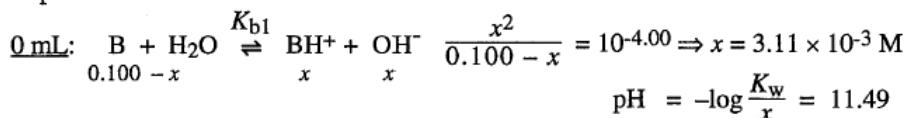


The pH of the initial solution before base is added is determined by the first acid dissociation reaction of H_2A . As base is added, it converts H_2A into an equivalent amount of HA^- . The buffer consisting of H_2A and HA^- governs the pH. At the first equivalence point, we have a solution of "pure" HA^- , the intermediate form of a diprotic acid. The pH is determined by the competitive acid and base reactions of HA^- . Between the two equivalence points there is a mixture of HA^- and A^{2-} , which is another

buffer. At the second equivalence point, we have converted all HA^- into A^{2-} , whose base hydrolysis reaction determines the pH. After the second equivalence point, the excess OH^- added from the buret is mainly responsible for determining the pH, with negligible contribution from A^{2-} .

12-23.	V_a	0	1	5	9	10	11	15	19	20	22
	pH	11.49	10.95	10.00	9.05	8.00	6.95	6.00	5.05	3.54	1.79

Representative calculations:



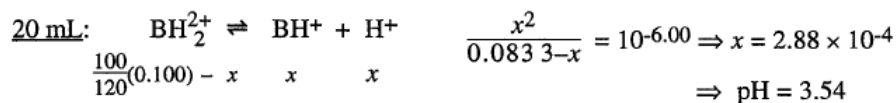
$$\underline{1 \text{ mL:}} \quad \text{pH} = \text{p}K_{\text{BH}^+} + \log \frac{[\text{B}]}{[\text{BH}^+]} = 10.00 + \log \frac{9}{1} = 10.95$$

10 mL: Predominant form is BH^+ with formal concentration $\frac{100}{110}(0.100) = 0.0909 \text{ M}$

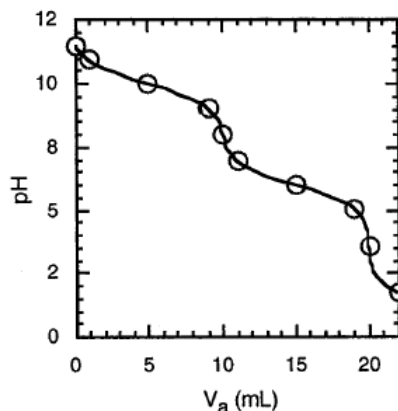
$$[\text{H}^+] \approx \sqrt{\frac{10^{-6.00} 10^{-10.00} (0.0909) + 10^{-6.00} 10^{-14.00}}{10^{-6.00} + 0.0909}}$$

$$= 1.00 \times 10^{-8} \Rightarrow \text{pH} = 8.00$$

$$\underline{11 \text{ mL:}} \quad \text{pH} = \text{p}K_{\text{BH}_2^+} + \log \frac{[\text{BH}^+]}{[\text{BH}_2^+]} = 6.00 + \log \frac{9}{1} = 6.95$$

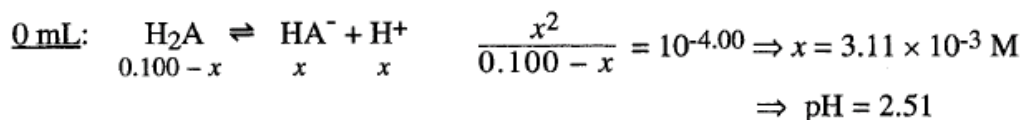


$$\underline{22 \text{ mL:}} \quad [\text{H}^+] = \left(\frac{2}{122}\right)(1.00) = 1.64 \times 10^{-2} \text{ M} \Rightarrow \text{pH} = 1.79$$



12-24.	V_b	0	1	5	9	10	11	15	19	20	22
	nH	2.51	3.05	4.00	4.95	6.00	7.05	8.00	8.95	10.46	12.21

Representative calculations:



$$\underline{1 \text{ mL:}} \quad \text{pH} = \text{p}K_1 + \log \frac{[\text{HA}^-]}{[\text{H}_2\text{A}]} = 4.00 + \log \frac{1}{9} = 3.05$$

10 mL: Predominant form is HA^- with formal concentration $\left(\frac{100}{110}\right)(0.100) = 0.0909 \text{ M}$.

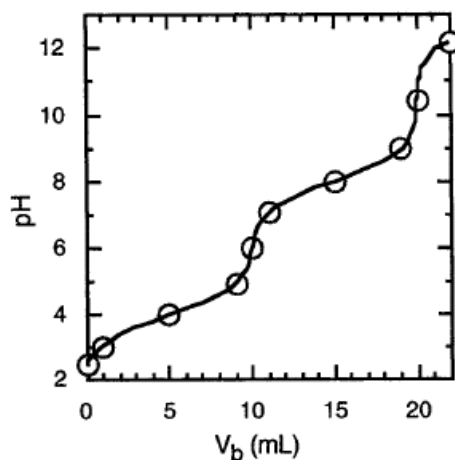
$$[\text{H}^+] \approx \sqrt{\frac{10^{-4.00} 10^{-8.00} (0.0909) + 10^{-4.00} 10^{-14.00}}{10^{-4.00} + 0.0909}}$$

$$= 9.99 \times 10^{-7} \Rightarrow \text{pH} = 6.00$$

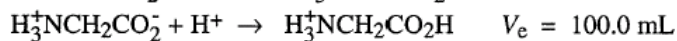
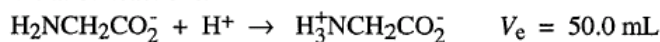
11 mL: $\text{pH} = \text{p}K_2 + \log \frac{[\text{A}^{2-}]}{[\text{HA}^-]} = 8.00 + \log \frac{1}{9} = 7.05$

20 mL: $\text{A}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HA}^- + \text{OH}^-$ $\frac{x^2}{\left(\frac{100}{120}\right)(0.100) - x} = \frac{K_w}{K_2} \Rightarrow x = 2.88 \times 10^{-4} \text{ M}$
 $\text{pH} = -\log \frac{K_w}{x} = 10.46$

22 mL: $[\text{OH}^-] = \left(\frac{2}{122}\right)(1.00) = 1.64 \times 10^{-2} \text{ M} \Rightarrow \text{pH} = 12.21$

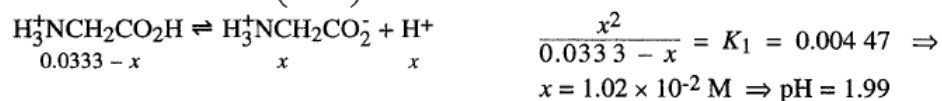


12-27. (a) Titration reactions:



At the second equivalence point the formal concentration of

$$\text{H}_3^+\text{NCH}_2\text{CO}_2\text{H} \text{ is } \left(\frac{50.0}{150.0}\right)(0.100) = 0.333 \text{ M}$$



(b) At $V_a = 90.0 \text{ mL}$, the approximation gives $\text{pH} = \text{p}K_1 + \log \frac{[\text{HG}]}{[\text{H}_2\text{G}^+]} = 2.35 +$

$\log \frac{1}{4} = 1.75$, which is lower than the correct value at 100.0 mL. At $V_a = 101.0$

mL, the approximation gives $[\text{H}^+] = \left(\frac{1.0}{151.0}\right)(0.100) = 6.62 \times 10^{-4} \text{ M} \Rightarrow$

$\text{pH} = 3.18$, which is higher than the correct value at 100.0 mL.

12-36. The quotient $[\text{HIn}]/[\text{In}^-]$ changes from 10:1 when $\text{pH} = \text{p}K_{\text{HIn}} - 1$ to 1:10 when $\text{pH} = \text{p}K_{\text{HIn}} + 1$. This change is generally sufficient to cause a complete color change.

12-37. The indicator has its acidic color when $\text{pH} = \text{p}K_{\text{HIn}} - 1$ because HIn is the dominant species. The indicator has its basic color when $\text{pH} = \text{p}K_{\text{HIn}} + 1$ because In^- is the dominant species. The color changes from the acidic color to the intermediate color to the basic color as the pH rises through the range $\text{p}K_{\text{HIn}} - 1$ to $\text{p}K_{\text{HIn}} + 1$. If the indicator is chosen correctly for the titration, this indicator pH transition range coincides with the steep part of the titration curve. The color change occurs near the equivalence point, which is the center of the steep portion of the titration curve.

12-47. Grams of cleaner titrated = $\left(\frac{4.373}{10.231 + 39.466}\right)(10.231 \text{ g}) = 0.9003 \text{ g}$

$$\text{mol HCl used} = \text{mol NH}_3 \text{ present} = (0.01422 \text{ L})(0.1063 \text{ M}) = 1.512 \text{ mmol}$$

$$1.512 \text{ mmol NH}_3 = 25.74 \text{ mg NH}_3$$

$$\text{wt\% NH}_3 = \frac{2.574 \times 10^{-2} \text{ g}}{0.9003 \text{ g}} \times 100 = 2.859\%$$