- Figure 10-4 shows the fractions α_{H2A}, α_{HA-}, α_{A2-} and for fumaric acid,

  → whose two pKa values are only 1.46 units apart.

- α_{HA-} rises only to 0.73 because the two pK values are so close together.

- In the region $pK_1 < pH < pK_2$.

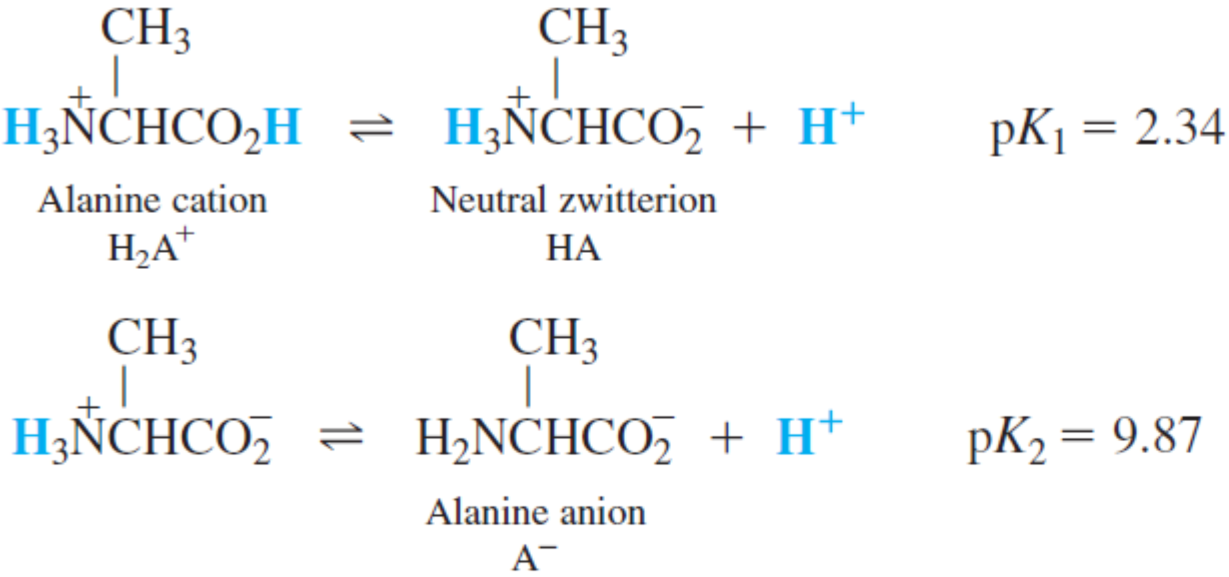
  → there are substantial quantities of H_2A and A^{2-}

See Fig 10-4

10.6 Isoelectric and Isoionic pH

- The isoelectric or isoionic pH of polyprotic molecules, such as proteins.

  → a diprotic system such as the amino acid alanine.



$$\mathrm{H_3\overset{+}{N}\overset{\overset{CH_3}{|}}{C}HCO_2H} \rightleftharpoons \mathrm{H_3\overset{+}{N}\overset{\overset{CH_3}{|}}{C}HCO_2^-} + \mathrm{H^+} \qquad \mathrm{p}K_1 = 2.34$$

Alanine cation H_2A^+ ; Neutral zwitterion HA

$$\mathrm{H_3\overset{+}{N}\overset{\overset{CH_3}{|}}{C}HCO_2^-} \rightleftharpoons \mathrm{H_2N\overset{\overset{CH_3}{|}}{C}HCO_2^-} + \mathrm{H^+} \qquad \mathrm{p}K_2 = 9.87$$

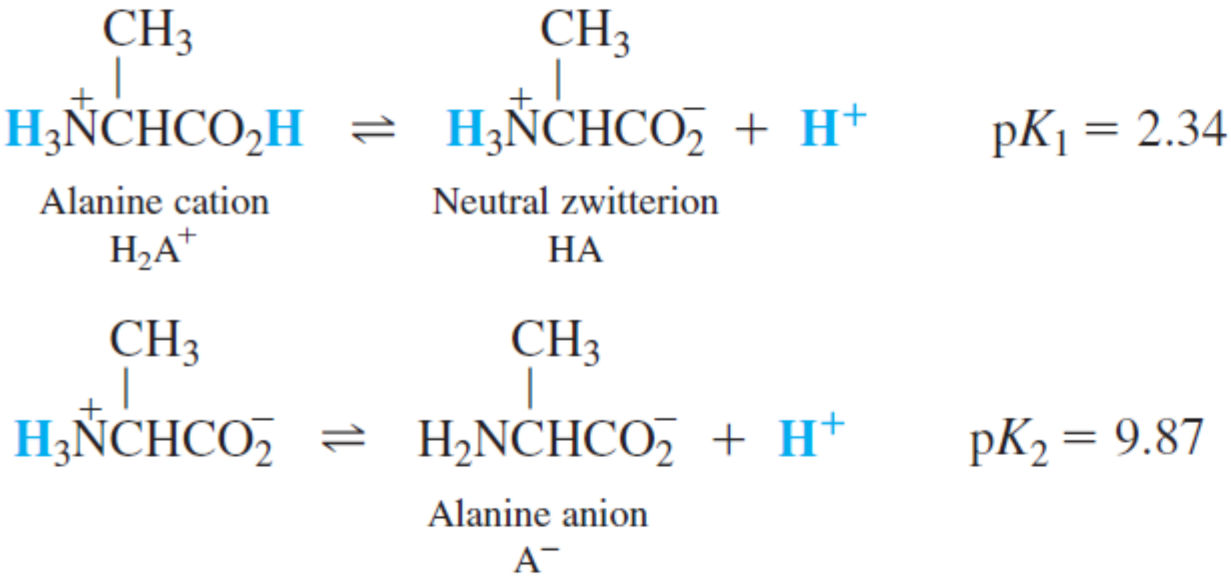
Alanine anion A^-

- **Isoionic pH**

  → the pH of the pure, neutral, polyprotic acid.

- **Isoelectric pH**

  → the pH at which average charge of the polyprotic acid is 0.



$$\mathrm{H_3\overset{+}{N}\overset{\overset{\textstyle CH_3}{|}}{C}HCO_2H} \rightleftharpoons \mathrm{H_3\overset{+}{N}\overset{\overset{\textstyle CH_3}{|}}{C}HCO_2^-} + \mathrm{H^+} \qquad \mathrm{p}K_1 = 2.34$$

Alanine cation H_2A^+ — Neutral zwitterion HA

$$\mathrm{H_3\overset{+}{N}\overset{\overset{\textstyle CH_3}{|}}{C}HCO_2^-} \rightleftharpoons \mathrm{H_2N\overset{\overset{\textstyle CH_3}{|}}{C}HCO_2^-} + \mathrm{H^+} \qquad \mathrm{p}K_2 = 9.87$$

Alanine anion A^-

- **Isoionic point (or isoionic pH)**

  → the pH obtained when the pure, neutral polyprotic acid HA (the neutral zwitterion) is dissolved in water.

- The only ions are H_2A^+, A^-, H^+, and OH^-.
- Most alanine is in the form HA
- The concentrations of H_2A^+ and A^- are **not equal** to each other.

- When alanine is dissolved in water,

  → the pH of the solution, by definition, is the isoionic pH.

- Because alanine (HA) is the intermediate form of the diprotic acid, H_2A^+,

  → $[H^+]$ is given by

Isoionic point:

$$[H^+] = \sqrt{\frac{K_1K_2F + K_1K_w}{K_1 + F}}$$

  → where F is the formal concentration of alanine.

- For 0.10 M alanine, the isoionic pH is found from

$$[H^+] = \sqrt{\frac{K_1K_2(0.10) + K_1K_w}{K_1 + (0.10)}} = 7.7 \times 10^{-7}\ \mathrm{M} \Rightarrow \mathrm{pH} = 6.11$$

- From $[H^+]$, K_1, and K_2,

  → calculate $[H_2A^+] = 1.68 \times 10^{-5}$ M

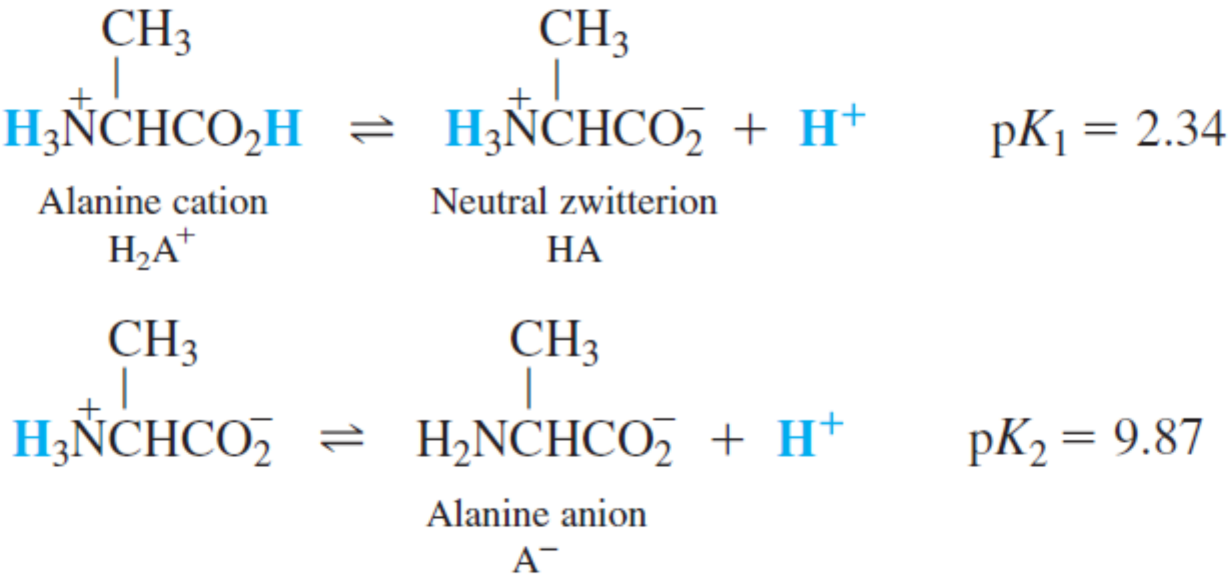
  $[A^-] = 1.76 \times 10^{-5}$ M   for pure alanine in water

  (the isoionic solution)

- There is a slight excess of A^-

  → because HA is a slightly stronger acid than it is a base.

  → HA dissociates to make A^- a little more than it reacts with water to make H_2A^+.



$$H_3\overset{+}{N}\overset{\overset{CH_3}{|}}{C}HCO_2H \rightleftharpoons H_3\overset{+}{N}\overset{\overset{CH_3}{|}}{C}HCO_2^- + H^+ \qquad pK_1 = 2.34$$

Alanine cation H_2A^+

Neutral zwitterion HA

$$H_3\overset{+}{N}\overset{\overset{CH_3}{|}}{C}HCO_2^- \rightleftharpoons H_2N\overset{\overset{CH_3}{|}}{C}HCO_2^- + H^+ \qquad pK_2 = 9.87$$

Alanine anion A^-

- **Isoelectric point (or isoelectric pH)**

  → the pH at which the average charge of the polyprotic acid is 0.

- Most of the molecules are in the uncharged form HA
- The concentrations of H_2A^+ and A^- are equal to each other.

- The isoelectric point

  → the pH at which $[H_2A^+] = [A^-]$

  → therefore, the average charge of alanine is 0.

- To go from the isoionic solution (pure HA in water) to the isoelectric solution,

  → we could add just enough strong acid to decrease $[A^-]$ and increase $[H_2A^+]$ until they are equal.

- Adding acid necessarily lowers the pH.

  → For alanine, the isoelectric pH must be lower than the isoionic pH.

- We calculate the isoelectric pH

  → by first writing expressions for $[H_2A^+]$ and $[A^-]$

$$[\mathrm{H_2A^+}] = \frac{[\mathrm{HA}][\mathrm{H^+}]}{K_1} \qquad [\mathrm{A^-}] = \frac{K_2[\mathrm{HA}]}{[\mathrm{H^+}]}$$

- Setting $[H_2A^+] = [A^-]$, we find

$$\frac{[\mathrm{HA}][\mathrm{H^+}]}{K_1} = \frac{K_2[\mathrm{HA}]}{[\mathrm{H^+}]} \Rightarrow [\mathrm{H^+}] = \sqrt{K_1K_2}$$

Isoelectric point:

$$\mathrm{pH} = \frac{1}{2}(\mathrm{p}K_1 + \mathrm{p}K_2)$$

- For a diprotic amino acid,

  → the isoelectric pH is halfway between the two pK_a values.

  → the isoelectric pH of alanine is ½(2.34 + 9.87) = 6.10.

Analytical Chemistry

Chapter 11. Acid-Base Titrations

In this chapter,

→ We learn to predict the shapes of titration curves and to find end points

→ How to deduce the quantities and pK_a values of acidic and basic substances in a mixture from an acid-base titration curve

11.1 Titration of Strong Base with Strong Acid

- For each type of titration in this chapter, our goal is

  → to construct a graph showing how pH changes as titrant is added.

  i) Titration of Strong Base with Strong Acid

  ii) Titration of Weak Acid with Strong Base

  iii) Titration of Weak Base with Strong Acid

- Can understand what is happening during the titration
- Can interpret an experimental titration curve.

11.1 Titration of Strong Base with Strong Acid

- The first step in each case

  → to write the chemical reaction between titrant and analyte.

- Then use that reaction to calculate **the composition and pH** after each addition of titrant.

- As a simple example,

  → let's focus on the titration of 50.00 mL of 0.020 00 M KOH with 0.100 0 M HBr.

  → the chemical reaction between titrant and analyte is merely

$$H^+ + OH^- \rightarrow H_2O \qquad K = 1/K_w = 10^{14}$$

- Because the equilibrium constant for this reaction is 10^{14},

  → it is fair to say that it “goes to completion.”

  → any amount of H^+ added will consume a stoichiometric amount of OH^-.

- It is useful to know the volume of HBr (V_e) needed to reach the equivalence point,

  → which we find by equating moles of KOH being titrated to moles of added HBr:

$$\underbrace{(V_e\,(\cancel{L}))\left(0.100\,0\,\frac{\text{mol}}{\cancel{L}}\right)}_{\substack{\text{mol of HBr}\\ \text{at equivalence point}}} = \underbrace{(0.050\,00\,\cancel{L})\left(0.020\,00\,\frac{\text{mol}}{\cancel{L}}\right)}_{\substack{\text{mol of OH}^-\\ \text{being titrated}}} \Rightarrow V_e = 0.010\,00\text{ L}$$

$$\underbrace{(V_e\,(\text{mL}))(0.100\,0\text{ M})}_{\substack{\text{mmol of HBr}\\ \text{at equivalence point}}} = \underbrace{(50.00\text{ mL})(0.020\,00\text{ M})}_{\substack{\text{mmol of OH}^-\\ \text{being titrated}}} \Rightarrow V_e = 10.00\text{ mL}$$

$$\underbrace{(V_e\,(\text{mL}))(0.100\,0\text{ M})}_{\substack{\text{mmol of HBr}\\ \text{at equivalence point}}} = \underbrace{(50.00\text{ mL})(0.020\,00\text{ M})}_{\substack{\text{mmol of OH}^-\\ \text{being titrated}}} \Rightarrow V_e = 10.00\text{ mL}$$

- When 10.00 mL of HBr have been added,

  → the titration is complete.

- Prior to this point,

  → there is excess, unreacted OH^- present.

- After V_e,

  → there is excess H^+ in the solution.

- In the titration of any strong base with any strong acid,

  → there are three regions of the titration curve that require different kinds of calculations:

1. Before the equivalence point,

   → the pH is determined by excess OH^- in the solution.

2. At the equivalence point,

   → H^+ is just sufficient to react with all OH^- to make H_2O.

   → The pH is determined by dissociation of water.

3. After the equivalence point,

   → pH is determined by excess H^+ in the solution.

- We will do one sample calculation for each region.

Region 1: Before the Equivalence Point

- When 3.00 mL of 0.1 M HBr have been added to 50.00 mL of 0.02 M NaOH,

  → the total volume is 53.00 mL.

  → HBr is consumed by NaOH, leaving excess NaOH.

- The moles of added HBr

  → (0.100 0 M)(0.003 00 L) = 0.300×10^{-3} mol HBr = 0.300 mmol HBr.

- The initial moles of NaOH

  → (0.020 00 M)(0.050 00 L) = $1.000 = 10^{-3}$ mol NaOH = 1.000 mmol NaOH.

- Unreacted OH^-

  → the difference 1.000 mmol - 0.300 mmol = 0.700 mmol

- The concentration of unreacted OH^-

  → (0.700 mmol)/(53.00 mL) = 0.013 2 M

- So, $[H^+] = K_w/[OH^-] = 7.57 \times 10^{-13}$ M

  → $pH = -\log[H^+] = 12.12$.

Region 2: At the Equivalence Point

- Region 2 is the equivalence point

  → where just enough H^+ has been added to consume OH^-.

- We could prepare the same solution by dissolving KBr in water.

- pH is determined by dissociation of water:

$$\mathrm{H_2O} \rightleftharpoons \underset{x}{\mathrm{H}^+} + \underset{x}{\mathrm{OH}^-}$$

$$K_w = x^2 \Rightarrow x = 1.00 \times 10^{-7}\ \mathrm{M} \Rightarrow \mathrm{pH} = 7.00$$

→ The pH at the equivalence point in the titration of any strong base (or acid) with strong acid (or base) will be 7.00 at 25°C.

- We will soon discover that

  → the pH is not 7.00 at the equivalence point in the titration of weak acids or bases.

- The pH is 7.00 only if the titrant and analyte are both strong.

Region 3: After the Equivalence Point

- Beyond the equivalence point,

  → we are adding excess HBr to the solution.

  → After the equivalence point, there is excess H^+.

Region 3: After the Equivalence Point

- The concentration of excess H^+ at, say, 10.50 mL is given by

$$[\mathrm{H^+}] = \underbrace{(0.100\,0\ \mathrm{M})}_{\substack{\text{Initial}\\ \text{concentration}\\ \text{of H}^+}} \underbrace{\left(\frac{\overset{\substack{\text{Volume of}\\ \text{excess H}^+}}{0.50}}{\underset{\substack{\text{Total volume}\\ \text{of solution}}}{50.00 + 10.50}}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 8.26 \times 10^{-4}\ \mathrm{M}$$

$$\mathrm{pH} = -\log[\mathrm{H^+}] = 3.08$$

- At $V_a = 10.50$ mL,

→ there is an excess of just $V_a - V_e = 10.50 - 10.00 = 0.50$ mL of HBr.

→ That is the reason why 0.50 appears in the dilution factor.

The Titration Curve

- Complete results are shown in Table 11-1 and Figure 11-1.

See Table 11-1

See Figure 11-1

- The titration curve in Figure 11-1 exhibits a rapid change in pH near the equivalence point.

- The equivalence point
  → where the slope (dpH/dV_a) is greatest
  → the second derivative is 0
  → which makes it an inflection point

See Figure 11-1

- As a reminder, the equivalence point occurs when added titrant is exactly enough for stoichiometric reaction with the analyte.

- The equivalence point is the ideal result we seek in a titration.

- What we actually measure is the end point
  → which is marked by a sudden physical change,
  → such as indicator color or an electrode potential

11.2 Titration of Weak Acid with Strong Base

- The **titration of 50.00 mL of 0.020 00 M MES with 0.100 0 M NaOH**.

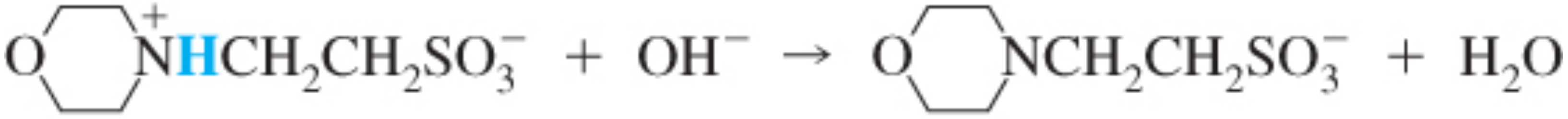
  → MES is an abbreviation for 2-(N-morpholino)ethanesulfonic acid

  → MES is a weak acid with $pK_a = 6.27$.

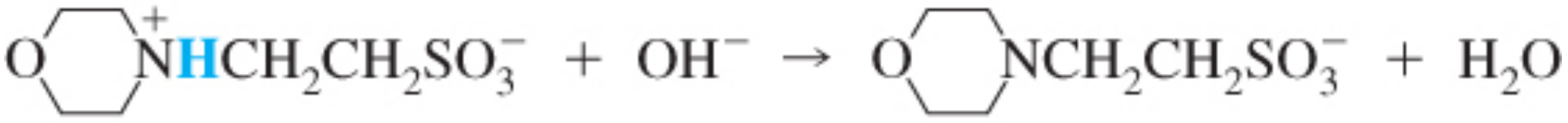
- Always **start by** writing the titration reaction.

  → The titration reaction is

(11-2)



HA **A^-**



HA **A^-** **(11-2)**

- Reaction 11-2 is the **reverse of the K_b reaction** for the base A^-.

  → the equilibrium constant for Reaction 11-2 is

  $$K = 1/K_b = 1/(K_w/K_a \text{ (for HA)}) = 5.4 \times 10^7.$$

- The equilibrium constant is **so large that** we can say that the reaction goes "to completion" after each addition of OH^-.

  → strong plus weak react completely.

- The titration calculations for this problem are of **four types**:

1. **Before any base is added**,

   → the solution contains just HA in water.

   → This is a weak acid whose pH is determined by the equilibrium

$$\mathrm{HA} \underset{}{\overset{K_a}{\rightleftharpoons}} \mathrm{H}^+ + \mathrm{A}^-$$

2. From the **first addition of NaOH until immediately before the equivalence point**,

   → there is a mixture of unreacted HA plus the A^- produced by Reaction 11-2.

   → We can use the Henderson-Hasselbalch equation to find the pH.

3. At the equivalence point,

→ "all" HA has been converted into A^-.

→ The same solution could have been made by dissolving A^- in water.

→ We have a weak base whose pH is determined by the reaction

$$A^- + H_2O \xrightleftharpoons{K_b} HA + OH^-$$

- Let's calculate the volume of base, V_b, needed to reach the equivalence point:

$$\underbrace{(V_b\,(\text{mL}))(0.100\,0\ \text{M})}_{\text{mmol of base}} = \underbrace{(50.00\ \text{mL})(0.020\,00\ \text{M})}_{\text{mmol of HA}} \Rightarrow V_b = 10.00\ \text{mL}$$

4. **Beyond the equivalence point**,

→ excess NaOH is being added to a solution of A^-.

→ To a good approximation, pH is determined by the strong base.

→ We calculate the pH as if we had simply added excess NaOH to water.

→ We neglect the tiny effect of A^-.

- We will do one sample calculation for each region.

Region 1: Before Base Is Added

- Before adding any base,

  → we have a solution of 0.020 00 M HA with pK_a = 6.27.

  → This is simply a weak-acid problem.

$$\underset{F - x}{HA} \rightleftharpoons \underset{x}{H^+} + \underset{x}{A^-} \qquad K_a = 10^{-6.27}$$

$$\frac{x^2}{0.020\,00 - x} = K_a \Rightarrow x = 1.03 \times 10^{-4} \Rightarrow pH = 3.99$$

Region 2: Before the Equivalence Point

- Adding OH^- creates a mixture of HA and A^-.

  → This mixture is a buffer

  → whose pH can be calculated with the Henderson-Hasselbalch equation from the quotient $[A^-]/[HA]$.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

- We only need relative concentrations

  → because pH depends on the quotient $[A^-]/[HA]$.

- Suppose we wish to calculate $[A^-]/[HA]$ when 3.00 mL of OH^- have been added.

- Because V_e = 10.00 mL,

  → we have added enough base to react with three-tenths of the HA.

- We can make a table showing the relative concentrations before and after the reaction:

Titration reaction:	HA	$+ OH^-$	$\rightarrow A^-$	$+ H_2O$
Relative initial quantities ($HA \equiv 1$)	1	$\frac{3}{10}$	—	—
Relative final quantities	$\frac{7}{10}$	—	$\frac{3}{10}$	—

- Once we know the quotient $[A^-]/[HA]$ in any solution, we know its pH:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right) = 6.27 + \log\left(\frac{3/10}{7/10}\right) = 5.90$$

- The point at which the volume of titrant is ½V_e is a special one in any titration.

Titration reaction:	HA	$+ OH^-$	$\rightarrow A^-$	$+ H_2O$
Relative initial quantities	1	$\frac{1}{2}$	—	—
Relative final quantities	$\frac{1}{2}$	—	$\frac{1}{2}$	—

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{1/2}{1/2}\right) = \mathrm{p}K_a$$

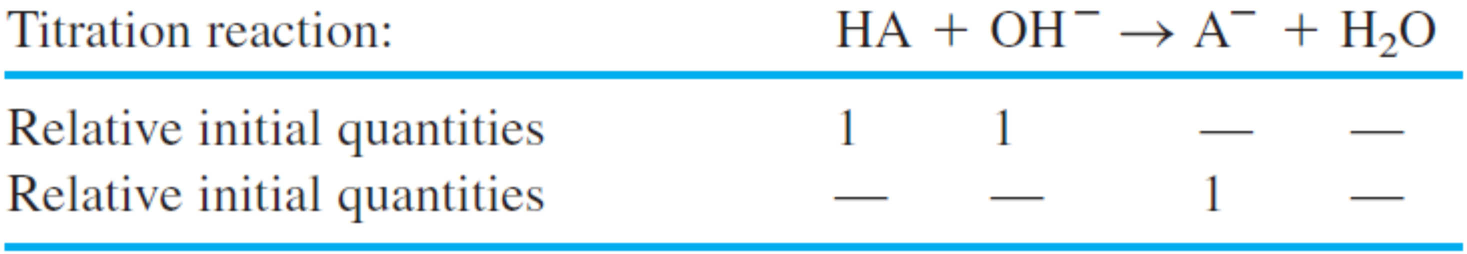
- When the volume of titrant is ½V_e, pH = pK_a for the acid HA (neglecting activity coefficients).
- From an experimental titration curve,

  → you can find the approximate value of pK_a by reading the pH when V_b = ½V_e,

  → V_b is the volume of added base.

Region 3: At the Equivalence Point

- At the equivalence point, there is exactly enough NaOH to consume HA.



Titration reaction:	HA	$+ OH^-$	$\rightarrow A^-$	$+ H_2O$
Relative initial quantities	1	1	—	—
Relative initial quantities	—	—	1	—

- At the equivalence point, HA has been converted into A^-, a weak base.

  → The solution contains "just" A^-.
- We could have prepared the same solution by dissolving the salt NaA in distilled water.
- A solution of NaA is merely a solution of a weak base.

- To compute the pH of a weak base, we write the reaction of the weak base with water:

$$\underset{F - x}{A^-} + H_2O \rightleftharpoons \underset{x}{HA} + \underset{x}{OH^-} \qquad K_b = \frac{K_w}{K_a}$$

- The only tricky point is that the formal concentration of A^- is no longer 0.020 00 M,
  → which was the initial concentration of HA.

- A^- has been diluted by NaOH:

Initial volume of HA

$$F' = \underbrace{(0.020\,00\ \text{M})}_{\substack{\text{Initial}\\ \text{concentration}\\ \text{of HA}}} \underbrace{\left(\frac{50.00}{50.00 + 10.00}\right)}_{\substack{\text{Dilution}\\ \text{factor}}} = 0.016\,7\ \text{M}$$

Total volume of solution

- With this value of F′, we can solve the problem:

$$\underset{F-x}{A^-} + H_2O \rightleftharpoons \underset{x}{HA} + \underset{x}{OH^-} \qquad K_b = \frac{K_w}{K_a}$$

$$\frac{x^2}{F' - x} = K_b = \frac{K_w}{K_a} = 1.86 \times 10^{-8} \Rightarrow x = 1.76 \times 10^{-5}\ \text{M}$$

$$\text{pH} = -\log[\text{H}^+] = -\log\left(\frac{K_w}{x}\right) = 9.25$$

- The pH at the equivalence point in this titration is 9.25.
  → It is not 7.00.
- The equivalence point pH will always be above 7 in the titration of a weak acid with a strong base,
  → because the acid is converted into its conjugate base at the equivalence point.