## **Weak Acid - Strong Base Titration** (Sec. 10-2)

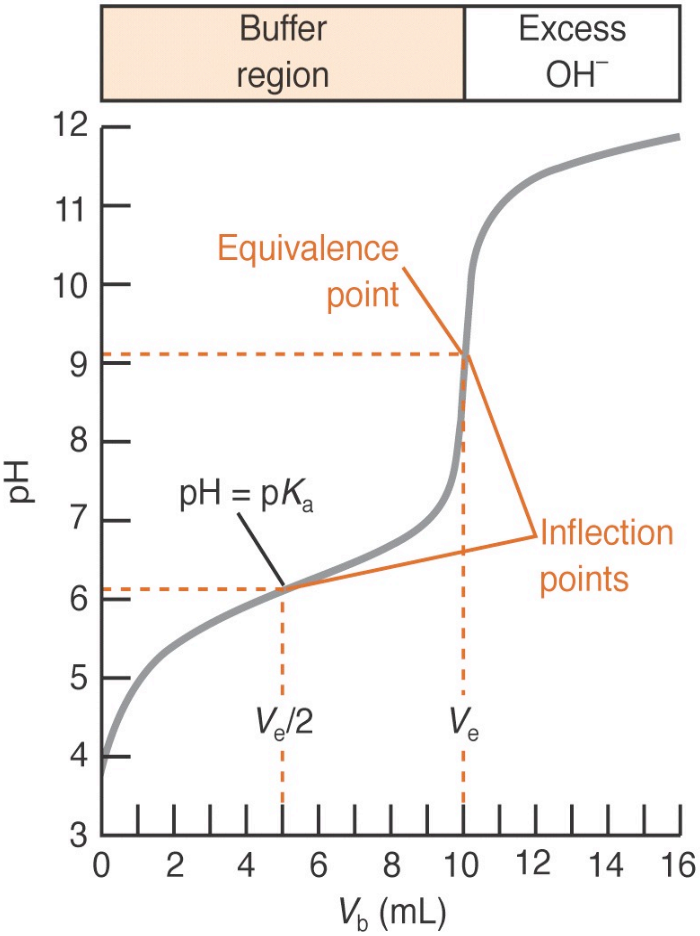
Four regions in titration curve:

1) Initial - only HA present
   $HA \rightleftharpoons H^+ + A^-$ controls pH

2) Before equiv. point – analyte is in excess, and all titrant creates $A^-$
   both HA & $A^-$ = buffer

3) Equiv. point – all analyte is $A^-$
   $A^- + H_2O \rightleftharpoons HA + OH^-$ controls pH

4) Past equivalence point – all analyte converted to $A^-$
   Calc conc. of excess strong base



**Example:** Calc the pH when 20.0 mL of 0.100 M $CH_3COOH$ (HAc, $K_a = 1.76 \times 10^{-5}$) is titrated with:

**a) 0 mL of 0.100 M NaOH**

Before addition of any NaOH, only HAc present

| | HAc | ⇌ | $H^+$ | + | $Ac^-$ |
|---|---|---|---|---|---|
| Initial: | 0.100 M | | 0 | | 0 |
| Change: | -X | | +X | | +X |
| Equil: | 0.100M – X | | X | | X |

$K_a = X\,X/(0.100M - X) = 1.76\times10^{-5}$
Since $K_a < 10^{-4} \Rightarrow X^2/0.100M = 1.76 \times 10^{-5}$
$X = 1.33\times10^{-3}\ M = [H^+]$

$pH = -\log(1.33\times10^{-3}\ M) = 2.876$

### b) 10.0 mL of 0.100 M NaOH

| | $HAc$ | + | $NaOH$ | → | $NaAc + H_2O$ |
|---|---|---|---|---|---|
| Initial: | $0.100M\times20.0mL$<br>$=2.00$ mmol | | $0.100M\times10.0mL$<br>$=1.00$ mmol | | 0 |
| Final: | $2.00 - 1.00$<br>$=1.00$ mmol | | 0 | | 1.00 mmol |

Solution contains HAc and NaAc $\Rightarrow$ buffer solution.

$C_{NaAc}$ = 1.00 mmol / (20.0 + 10.0) mL = 0.0333 M
$C_{HAc}$ = 1.00 mmol / (20.0 + 10.0) mL = 0.0333 M

$C_{NaAc}$ & $C_{HAc} > 10^{-3}$ M and $K_a = 1.76\times10^{-5} < 10^{-3}$ (approximation valid)

$pH = pK_a + \log C_{NaAc}/C_{HAc}$
$= -\log(1.76\times10^{-5}) + \log(0.0333M/0.0333M) = 4.754$

### c) 20.0 mL of 0.100 M NaOH

At equivalence point $\Rightarrow$ solution of $Ac^-$ (weak base)
$C_{Ac-} = 0.100M\times20.0mL / (20.0 + 20.0)$ mL = 0.0500 M
For a weak base, use base hydrolysis equilibrium

| | $Ac^-$ | + | $H_2O$ | = | $HAc$ | + | $OH^-$ |
|---|---|---|---|---|---|---|---|
| Initial: | 0.0500 M | | | | 0 | | 0 |
| Change | -X | | | | +X | | +X |
| Final: | 0.0500M – X | | | | X | | X |

$K_b = x^2/(0.0500 - x) = K_w/K_a = 10^{-14}/1.76\times10^{-5} = 5.68\times10^{-10}$
Since $K_b = 5.68\times10^{-10} < 10^{-4}$, so $x^2/0.0500M = 5.68\times10^{-10}$
$X = 5.33\times10^{-6} = [OH^-]$; $pH = 14 - pOH = 14 - 5.273 = 8.727$

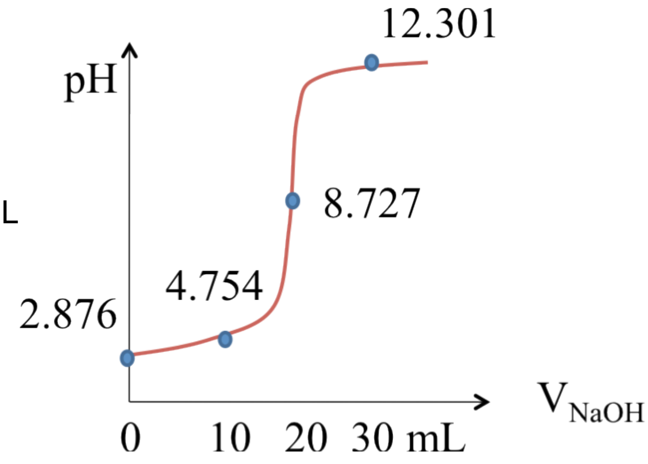
### d) 30.0 mL of 0.100 M NaOH

10.0 mL of NaOH past the equiv. point
pH determined by excess of strong base.

$C_{xs\ OH} = 10.0\ mL*0.100M / (20.0 + 30.0)$ mL
$= 0.0200$ M

$pOH = -\log 0.0200M = 1.699$

$pH = 14 - 1.699 = 12.301$



## **Weak Base - Strong Acid Titration** (Sec. 10-3)

e.g., $NH_3 + HCl \rightarrow NH_4Cl$

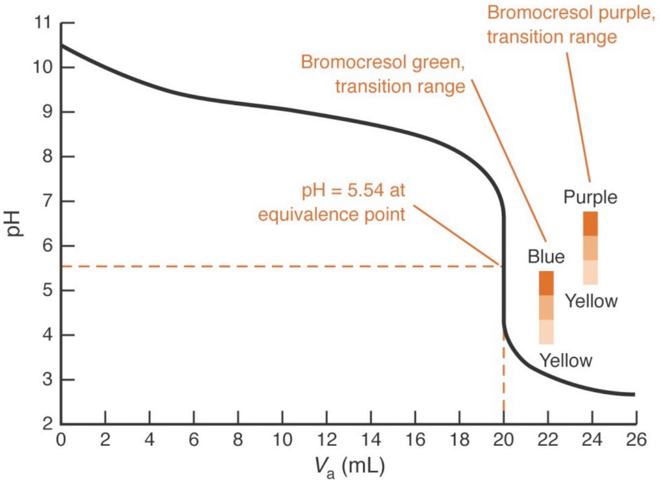
Four regions in titration curve:

1) Initial - only B present
   $B + H_2O \rightleftharpoons BH^+ + OH^-$ controls pH

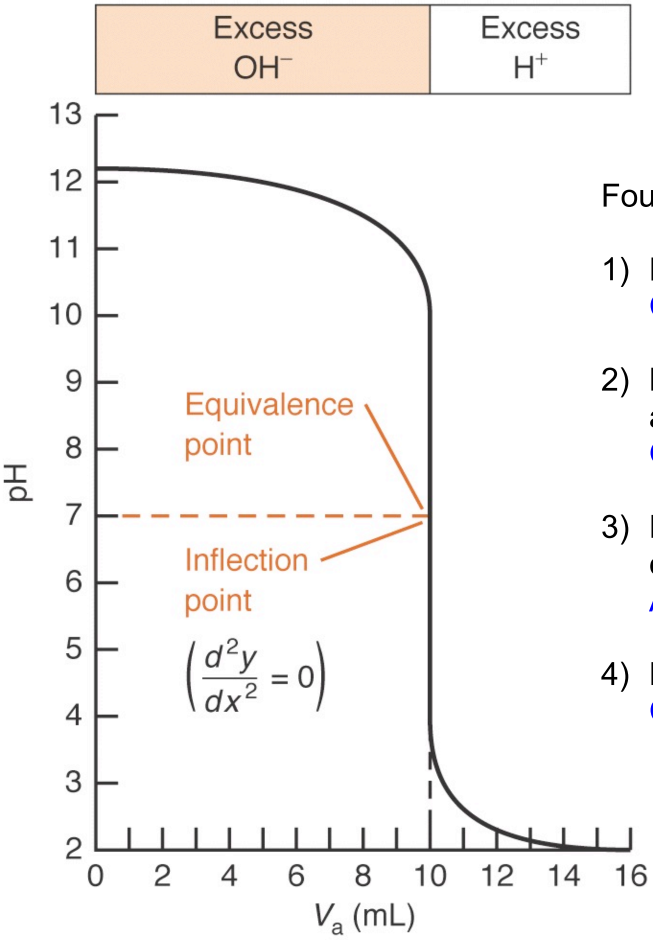
2) Before equiv. point – analyte is in excess, and all titrant creates B
   both $BH^+$ & B = buffer

3) Equiv. point – all analyte is $BH^+$
   $BH^+ \rightleftharpoons H^+ + B$ controls pH

4) Past equivalence point – all analyte converted to B
   Calc conc. of excess strong acid



## **Strong Base-Strong Acid Titration** (Sec. 10-1)



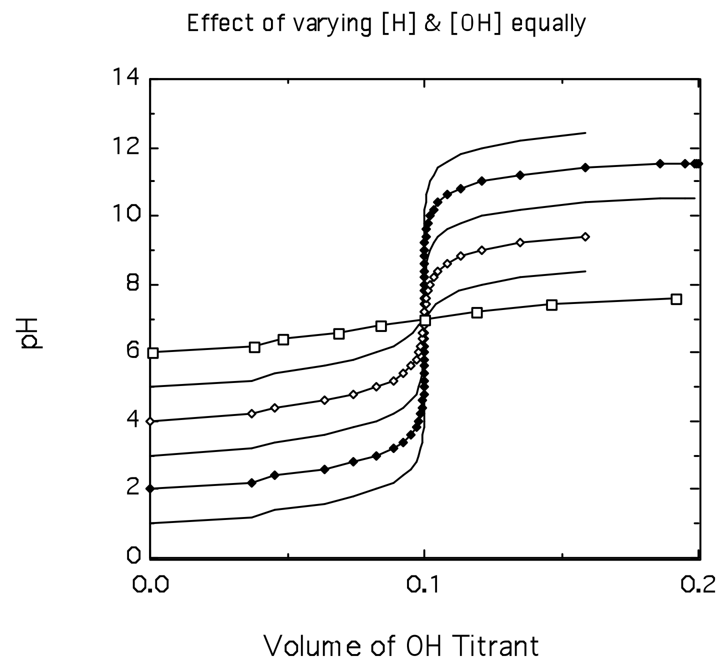
Four regions in titration curve:

1) Initial - analyte alone
   Calc $[OH^-]$ from [strong base]

2) Before equiv. point – all titrant reacts but analyte in excess. Calc conc. of remaining $OH^-$ from the strong base

3) Equiv. point – all analyte and titrant are consumed.
   Autoprotolysis ($H_2O$, pH=7)

4) Past equiv. point - titrant in xs
   Calc. $[H^+]$ from excess strong acid



**$C_{HCl}$ = $C_{NaOH}$**

0.1 M
0.01 M
0.001 M
0.1 mM
0.01 mM
0.001 mM

pH indicator
conc. limit $10^{-4}$ M for 1 ppt precision

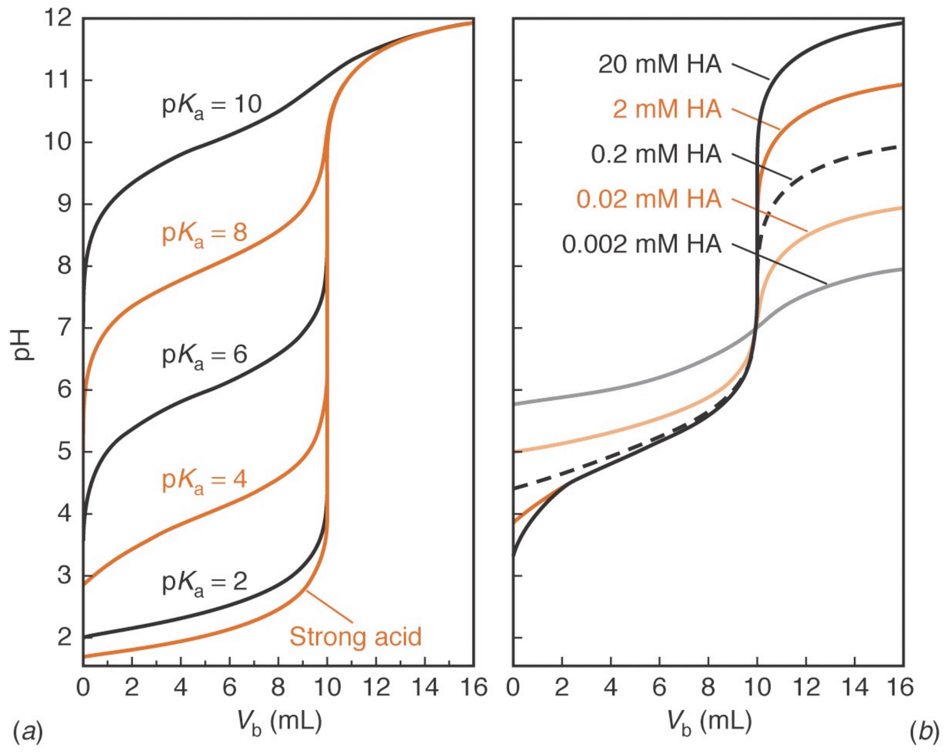
pH meter conc. limit $10^{-5}$ M

## Sharpness of weak acid – strong base titration

Two factors:
- $K_a$ affects the steepness d(pH)/d(volume)
- [analyte] and [titrant] affect ΔpH

50 mL of 0.02 M HA
With 0.1 M NaOH

50 mL of HA ($pK_a \approx 4.5$)
$[OH^-] = 5 \times [HA]$

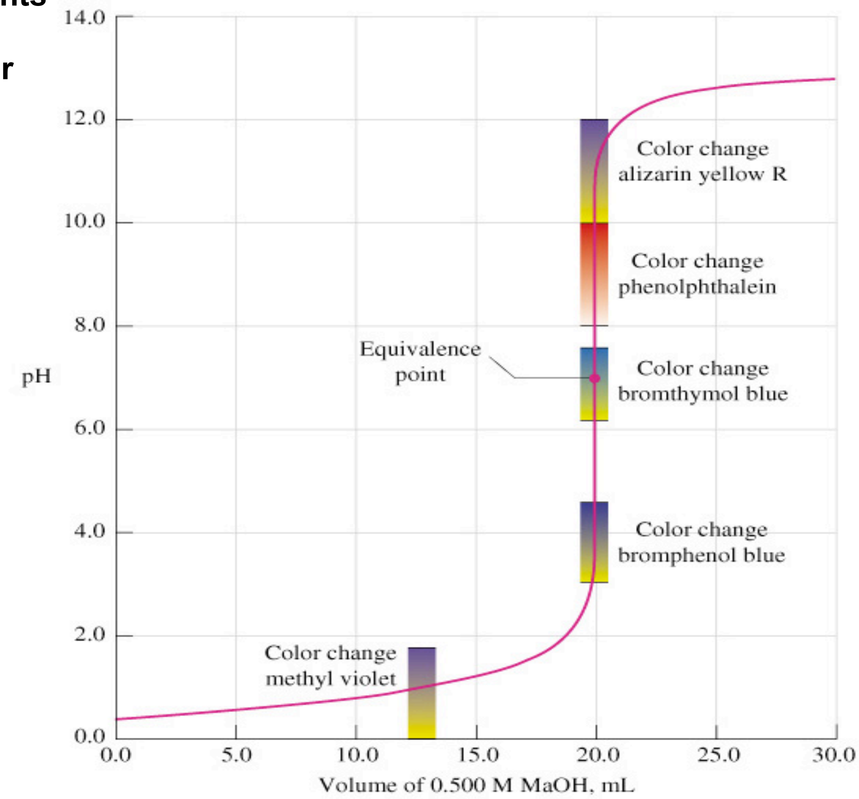


## Acid-Base Titration Endpoints

### Selection of visual indicator

Transition range $pK_a \pm 1$

Indicator Error

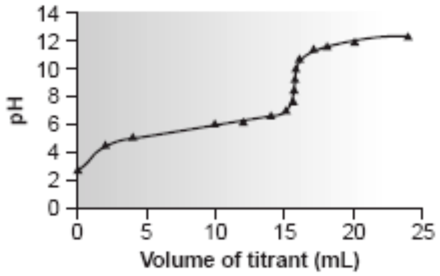


### pH meter

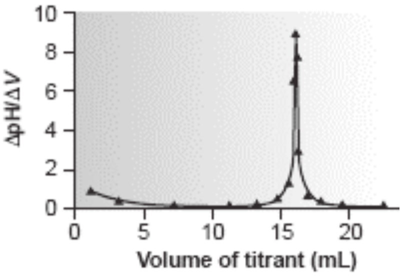
Using derivatives to find endpoint

Applicable for pH electrode use

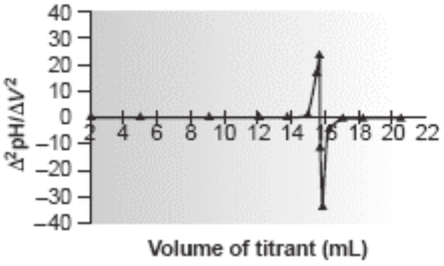
Needs a number of points close to the inflection point



Titration curve

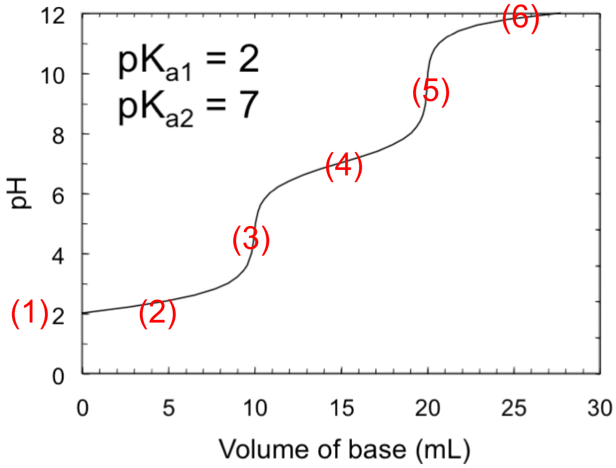


First derivative



Second derivative

## Diprotic Acid Titration Curve



1) Initial - analyte $H_2A$ alone is present
   $H_2A \rightleftharpoons H^+ + HA^-$ controls pH

2) Before equivalence point - analyte is in excess, and all titrant creates product $HA^-$;
   $H_2A$ & $HA^-$ together make a buffer

3) First equivalence point - essentially all $HA^-$
   amphoteric rxn of $HA^-$ controls pH

4) Past first equivalence point - titrant makes product $A^{2-}$ from $HA^-$
   Both $A^{2-}$ and $HA^-$ are present, making another buffer

5) Second Equivalence point - $A^{2-}$ is the predominant species, so it controls pH:
   $A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$ (base hydrolysis)

6) Past equivalence point - titrant is in excess, and all analyte HA turns into $A^{2-}$
   Calculate conc. of excess strong base

**Example:** Calc the pH of the solution resulting when 20.0 mL of 0.100 M diprotic acid ($H_2A$) has been titrated with 0, 5.00, 20.0, 35.0, 40.0 and 50.0 mL of 0.100 M NaOH. For $H_2A$, $K_{a1} = 1.00 \times 10^{-4}$ and $K_{a2} = 1.00 \times 10^{-8}$

**1) Before the addition of any titrant ($V_{NaOH} = 0$), only $H_2A$ present in the solution.**

Because $K_{a1}/K_{a2} = 1.00 \times 10^{-4} / 1.00 \times 10^{-8} = 1.00 \times 10^{4} >> 100$,
(we can neglect the 2nd hydrolysis)

| | $H_2A$ | = | $H^+$ | + | $HA^-$ |
|---|---|---|---|---|---|
| Initial: | 0.100 M | | 0 | | 0 |
| Final: | 0.100 – X | | X | | X |

$K_{a1} = X X /(0.100 - X) = 1.00\times10^{-4}$

Since $K_a \le 10^{-4}$
$X^2/0.100 = 1.00 \times 10^{-4}$
$X = 3.16\times10^{-3} = [H^+]$

$pH = - \log (3.16\times10^{-3}) = 2.500$

### 2) After 5.00 mL of NaOH added ($V_{NaOH}$ = 5.00 mL), there is a reaction.

| | $H_2A$ | + | NaOH | → | NaHA + $H_2O$ |
|---|---|---|---|---|---|
| Initial: | 0.100M×20.0mL<br>=2.00 mmol | | 0.100M×5.00mL<br>=0.500 mmol | | 0 |
| Final: | 2.00 – 0.500 m<br>=1.50 mmol | | 0 | | 0.500 mmol |

So after the rxn, the solution contains $H_2A$ and NaHA, a buffer solution ($H_2A \leftrightharpoons HA^- + H^+$, or $K_{a1}$)

$C_{NaHA}$ = 0.500 mmol / (20.0 + 5.00 ) mL = 0.0200 M
$C_{H2A}$ = 1.50 mmol / (20.0 + 5.00 ) mL = 0.0600 M

Since $C_{NaHA}$ & $C_{H2A} > 10^{-3}$ M and $K_{a1} = 1.00\times10^{-4} < 10^{-3}$, so
$pH = pK_{a1} + \log C_{NaHA} / C_{H2A} = -\log(1.00\times10^{-4}) + \log(0.0200/0.0600) = 3.520$

### 3) After 20.0 mL of NaOH added ($V_{NaOH}$ = 20.0 mL), there is a reaction.

| | $H_2A$ | + | NaOH | → | NaHA + $H_2O$ |
|---|---|---|---|---|---|
| Initial: | 0.100M×20.0mL<br>=2.00 mmol | | 0.100M×20.0mL<br>=2.00 mmol | | 0 |
| Final: | 0 | | 0 | | 2.00 mmol |

So after the rxn, the solution contains only NaHA, an amphiprotic salt; and this is the first equivalence points.

$C_{NaHA}$ = 2.00 mmol / (20.0 + 20.0 ) mL = 0.0500 M

For an amphiprotic salt, we use a special equation to calc pH.

$$[H^+] = \sqrt{\frac{K_{a1}K_{a2}[HA^-] + K_wK_{a1}}{K_{a1} + [HA^-]}}$$

Assume $[HA^-] = C_{NaHA}$ $$[H^+] = \sqrt{\frac{10^{-4} \text{ x } 10^{-8} \text{ x } 0.05 + 10^{-14} \text{ x } 10^{-4}}{10^{-4} + 0.05}}$$

$[H^+] = 1.00 \text{ x } 10^{-6}$ pH = 6.000

By the way, you could apply the approximately and get the same answer:
If $K_{a2}F \gg K_w$ and $K_{a1} \ll F$, then $[H^+] \cong \sqrt{K_{a1}K_{a2}}$

**4) After 35.0 mL of NaOH added ($V_{NaOH}$ = 35.0 mL), there is a reaction:**

| | $H_2A$ | + | NaOH | → | NaHA + $H_2O$ |
|---|---|---|---|---|---|
| Initial: | 0.100M×20.0mL<br>=2.00 mmol | | 0.100M×35.0mL<br>=3.50 mmol | | 0 |
| Final: | 0 | | 3.50 – 2.00 mmol<br>=1.50 mmol | | 2.00 mmol |

So after the rxn, the solution contains NaOH and NaHA – these two will react:

| | NaHA | + | NaOH | → | $Na_2A$ + $H_2O$ |
|---|---|---|---|---|---|
| Initial: | 2.00 mmol | | 1.50 mmol | | 0 |
| Final: | 2.00 – 1.50<br>=0.50 mmol | | 0 | | 1.50 mmol |

After the 2nd rxn, the solution contains NaHA and $Na_2A$, a buffer.

$C_{Na2A}$ = 1.50 mmol / (20.0 + 35.0 ) mL = 0.0273 M
$C_{NaHA}$ = 0.50 mmol / (20.0 + 35.0 ) mL = 0.00909 M

Since $C_{Na2A}$ & $C_{NaHA} > 10^{-3}$ M and $K_{a2} = 1.00\times10^{-8} < 10^{-3}$, so
$pH = pK_{a2} + \log C_{Na2A} / C_{NaHA} = -\log(1.00\times10^{-8}) + \log(0.0273/0.00909) = 8.477$

**5) After 40.0 mL of NaOH added ($V_{NaOH}$ = 40.0 mL), there is a reaction:**

| | $H_2A$ | + | NaOH | → | NaHA + $H_2O$ |
|---|---|---|---|---|---|
| Initial: | 0.100M×20.0mL<br>=2.00 mmol | | 0.100M×40.0mL<br>=4.00 mmol | | 0 |
| Final: | 0 | | 4.00 – 2.00 mmol<br>=2.00 mmol | | 2.00 mmol |

So after the rxn, the solution contains NaOH and NaHA – these two will react:

| | NaHA | + | NaOH | → | $Na_2A$ + $H_2O$ |
|---|---|---|---|---|---|
| Initial: | 2.00 mmol | | 2.00 mmol | | 0 |
| Final: | 0 | | 0 | | 2.00 mmol |

After the 2nd rxn, the solution contains $Na_2A$, a weak base.
$C_{Na2A}$ = 2.00 mmol / (20.0 + 40.0 ) mL = 0.0333 M
For a weak base, we use base hydrolysis equilibrium to calc pH.

| | $A^{2-}$ + $H_2O$ | = | $HA^-$ | + | $OH^-$ |
|---|---|---|---|---|---|
| Initial: | 0.0333 M | | 0 | | 0 |
| Final: | 0.0333 – X | | X | | X |

$K_{b1} = X\,X/(0.0333 - X) = K_w/K_{a2} = 10^{-14}/1.00\times10^{-8} = 1.00\times10^{-6}$
Since $K_{b1} = 1.00\times10^{-6} < 10^{-4}$, so $X^2/0.0333 = 1.00\times10^{-6}$
$X = 1.82\times10^{-4} = [OH^-]$, $pH = 14 - pOH = 14 - 3.737 = 10.263$

**6) After 50.0 mL of NaOH added ($V_{NaOH}$ = 50.0 mL), there is a reaction:**

| | $H_2A$ | + | NaOH | → | $NaHA + H_2O$ |
|---|---|---|---|---|---|
| Initial: | 0.100M×20.0mL<br>=2.00 mmol | | 0.100M×50.0mL<br>=5.00 mmol | | 0 |
| Final: | 0 | | 5.00 – 2.00<br>=3.00 mmol | | 2.00 mmol |

So after the rxn, the solution contains NaOH and NaHA – these two will react:

| | NaHA | + | NaOH | → | $Na_2A + H_2O$ |
|---|---|---|---|---|---|
| Initial: | 2.00 mmol | | 3.00 mmol | | 0 |
| Final: | 0 | | 3.00 – 2.00<br>= 1.00 mmol | | 2.00 mmol |

After the 2nd rxn, the solution contains NaOH and $Na_2A$, a strong base and a weak base. The solution pH is determined by the strong base conc.

$C_{NaOH}$ = 1.00 mmol / (20.0 + 50.0 ) mL = 0.0143 M
pOH = - log(0.0143) = 1.845 pH = 14 – 1.845 = 12.155

**Titration curve for this example:**