Acid-Base Titrations

Titration is a form of analysis in which we measure the volume of material of known concentration sufficient to react with the substance being analyzed.

Titration

a solution of known concentration, called a *standard solution* is added gradually to another solution of unknown concentration until the chemical reaction between the two solutions is complete

equivalence point

- **the exact number of moles required for the reaction**
- **detected by a color change in an *acid-base indicator* or electronically**

Acid-Base Titrations

How does the pH change during the course of the following kinds of titration?

strong acid-strong base

weak acid-strong base

weak base-strong acid

Titrations Involving a Strong Acid and a Strong Base

Titrations Involving a Strong Acid and a Strong Base

titrate 25.0 mL of 0.100 *M* HCl with 0.100 *M* NaOH

Note: $\frac{\text{mmol}}{\text{mL}}$ **and** $\frac{\text{mol}}{\text{L}}$

are equivalent

Titrations Involving a Strong Acid and a Strong Base

What is the pH after the addition of 10.0 mL of 0.100 *M* NaOH to 25.0 mL of 0.100 *M* HCl ?

$$HCl\ (aq) + NaOH(aq) \rightleftharpoons H_2O\ (l) + NaCl\ (aq)$$

$$H^+\ (aq) + OH^-\ (aq) \rightleftharpoons H_2O\ (l)$$

Titrations Involving a Strong Acid and a Strong Base

What is the pH after the addition of 10.0 mL of 0.100 *M* NaOH to 25.0 mL of 0.100 *M* HCl ?

$$10\text{ml} \times \frac{0.1\text{mmol NaOH}}{\text{mL}} = 1.0\text{mmol } OH^-$$

$$25\text{ml} \times \frac{0.1\text{mmol HCl}}{\text{mL}} = 2.5\text{mmol } H^+$$

$$H^+ (aq) + OH^- (aq) \rightleftharpoons H_2O (l)$$

	H^+	OH^-	H_2O
start	2.5mmol	1.0mmol	0
end	1.5mmol	0	1.0mmol

Titrations Involving a Strong Acid and a Strong Base

What is the pH after the addition of 10.0 mL of 0.100 *M* NaOH to 25.0 mL of 0.100 *M* HCl ?

$$H^+ (aq) + OH^- (aq) \rightleftharpoons H_2O (l)$$

$$[H^+] = \frac{1.5 \text{mmol } H^+}{35.0 \text{ mL (solution)}} = 4.28 \times 10^{-2} \text{ M}$$

pH = 1.37

Titrations Involving a Strong Acid and a Strong Base

What is the pH after the addition of 25.0 mL of 0.100 *M* NaOH to 25.0 mL of 0.100 *M* HCl ?

$$25\text{ml} \times \frac{0.1\text{mmol NaOH}}{\text{mL}} = 2.5\text{mmol } OH^-$$

$$25\text{ml} \times \frac{0.1\text{mmol HCl}}{\text{mL}} = 2.5\text{mmol } H^+$$

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

	H^+	OH^-	H_2O
start	2.5 mmol	2.5 mmol	0
end	0	0	2.5 mmol

Titrations Involving a Strong Acid and a Strong Base

What is the pH after the addition of 25.0 mL of 0.100 *M* NaOH to 25.0 mL of 0.100 *M* HCl ?

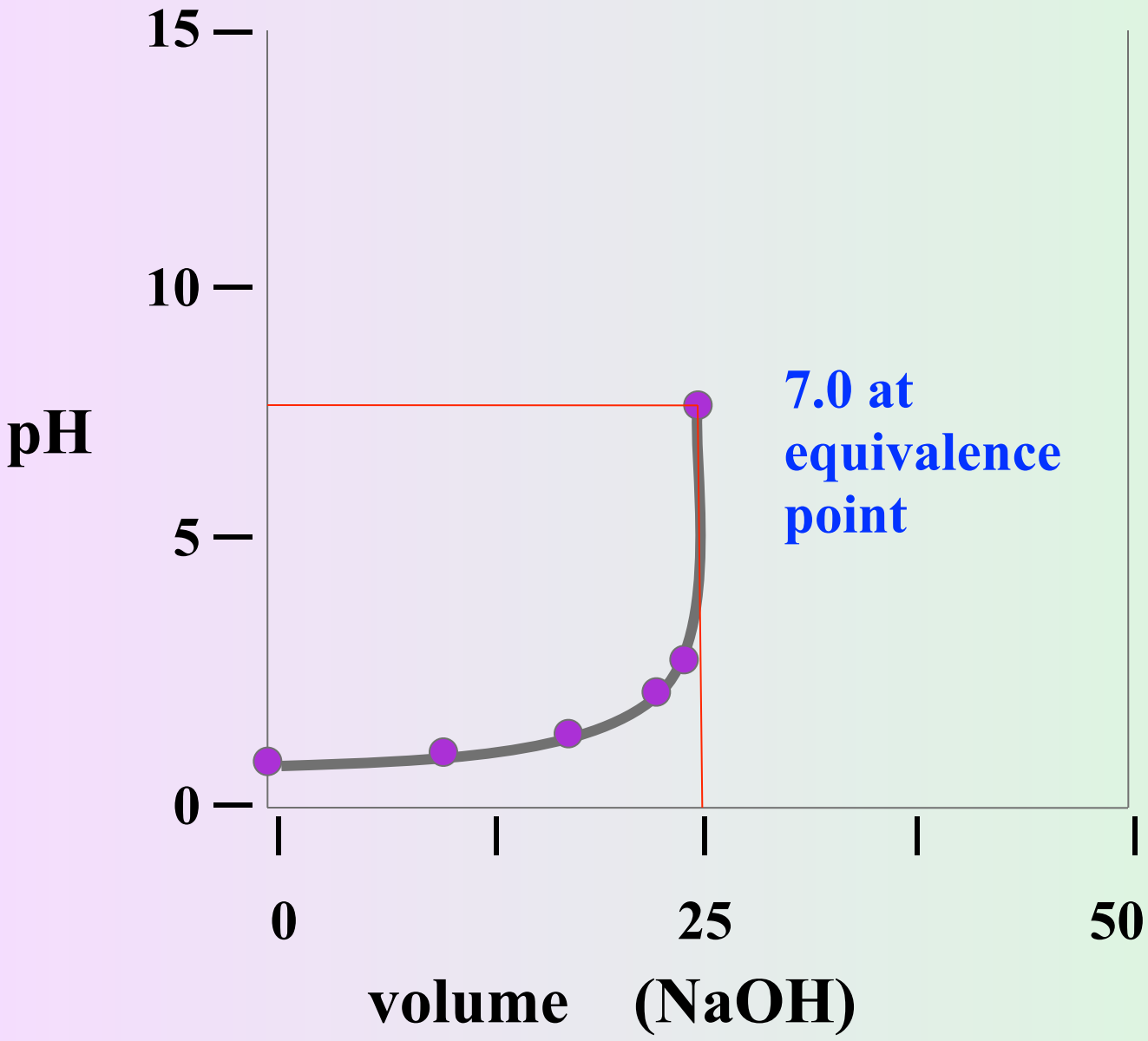
$$H_2O\,(l) + H_2O\,(l) \rightleftharpoons H_3O^+(aq) + OH^-\,(aq)$$

$$[H^+] = 1.0 \times 10^{-7}\ M$$

pH = 7.0

pH versus ml 0.10 M NaOH added

volume (NaOH)	volume (total)	mmol (HCl)	$[H^+]$ *M*	pH
0	25.0ml	2.5	0.10	1.00
10.0 ml	35.0 ml	1.5	0.043	1.37
20.0 ml	45.0 ml	0.5	0.011	1.95
24.0 ml	49.0 ml	0.1	0.002	2.69
24.5 ml	49.5 ml	0.05	0.001	3.00
25.0 ml	50.0 ml	0	10^{-7}	7.00



Titration of 25.00 ml of 0.100 *M* HCl with 0.100 *M* NaOH

Titrations Involving a Strong Acid and a Strong Base

What is the pH after the addition of 35.0 mL of 0.100 *M* NaOH to 25.0 mL of 0.100 *M* HCl ?

$$35\text{ml} \times \frac{0.1\text{mmol NaOH}}{\text{mL}} = 3.5\text{mmol } OH^-$$

$$25\text{ml} \times \frac{0.1\text{mmol HCl}}{\text{mL}} = 2.5\text{mmol } H^+$$

$$H^+(aq) + OH^-(aq) \rightleftharpoons H_2O(l)$$

	$H^+(aq)$	$OH^-(aq)$	$H_2O(l)$
start	2.5 mmol	3.5 mmol	0
end	0	1.0 mmol	2.5 mmol

Titrations Involving a Strong Acid and a Strong Base

What is the pH after the addition of 35.0 mL of 0.100 *M* NaOH to 25.0 mL of 0.100 *M* HCl ?

$$H^+ (aq) + OH^- (aq) \rightleftharpoons H_2O (l)$$

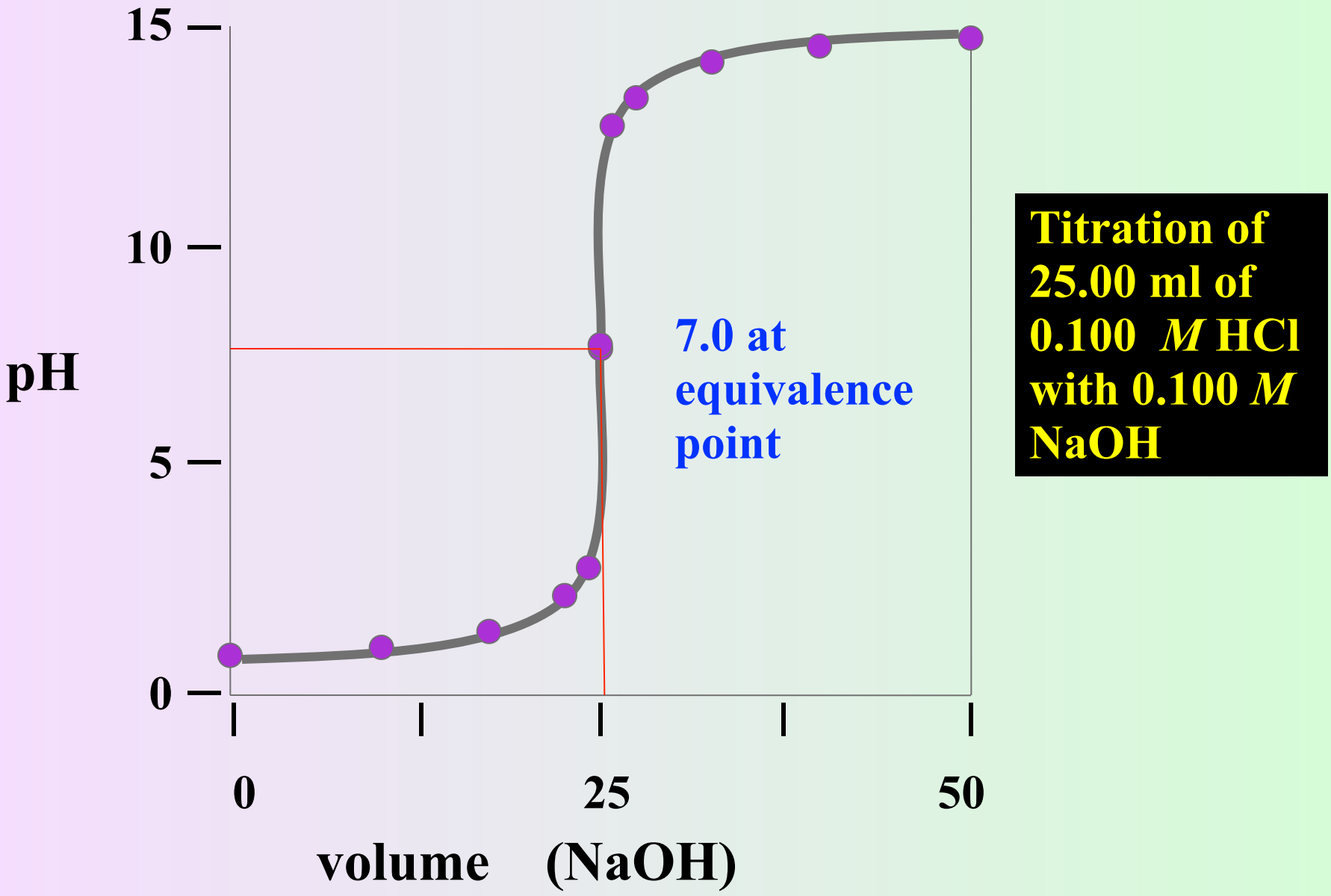
$$[OH^-] = \frac{1.0 \text{ mmol } OH^-}{60.0 \text{ mL (solution)}} = 1.66 \times 10^{-2} \text{ M}$$

$$pOH = 1.78$$

$$pH = 12.22$$

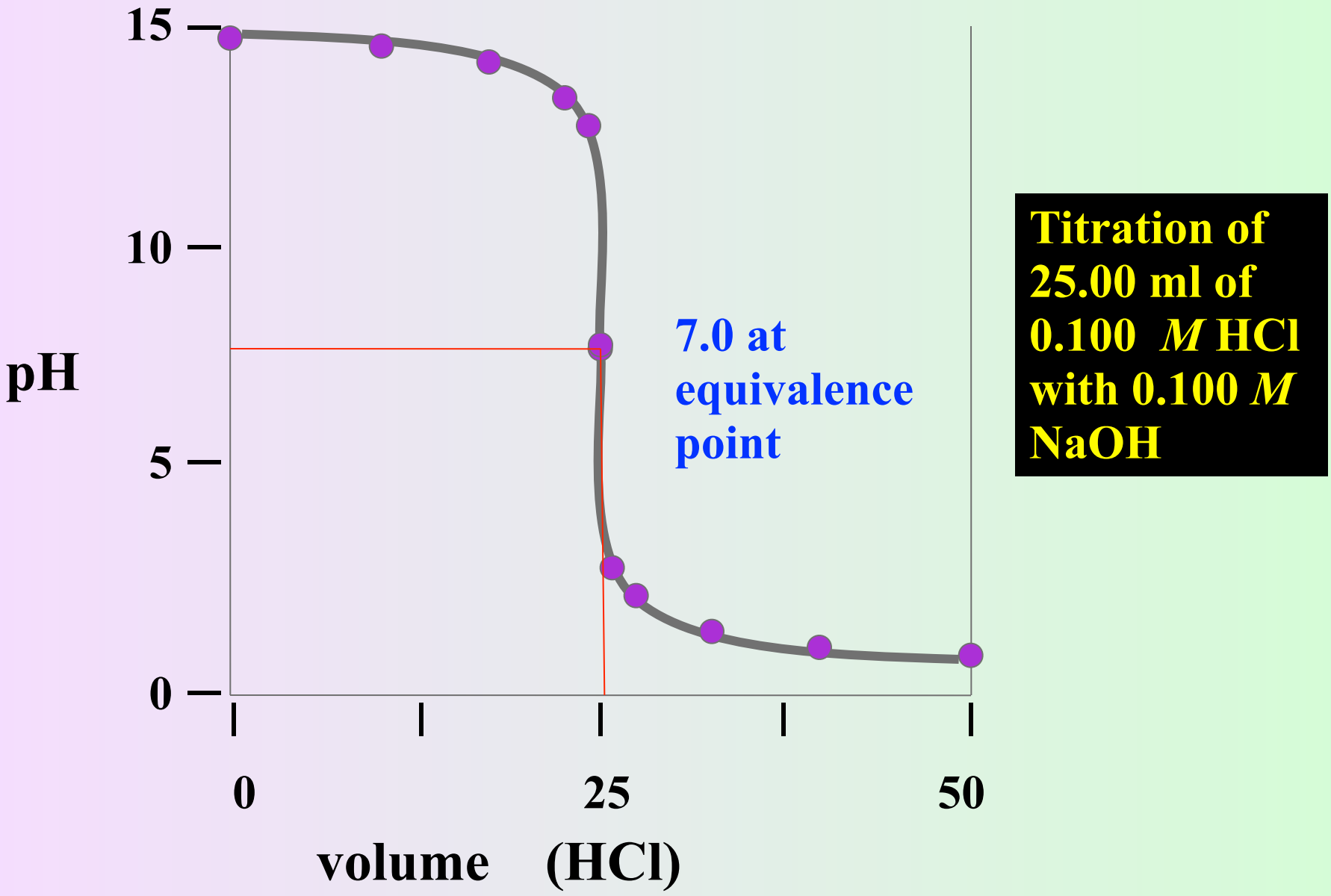
pH versus ml 0.10 M NaOH added

volume (NaOH)	volume (total)	mmol (HCl)	$[H^+]$ *M*	pH
25.0 ml	50.0ml	0	10^{-7}	7.00
		mmol (NaOH)	$[OH^-]$ *M*	
25.5 ml	50.5 ml	0.05	0.001	11.00
26.0 ml	51.5 ml	0.10	0.002	11.29
30.0 ml	55.0 ml	0.50	0.009	11.96
40.5 ml	65.0 ml	1.50	0.023	12.36
50.0 ml	75.0 ml	2.50	0.033	12.52


15
10
5
0
pH
7.0 at equivalence point
0
25
50
volume (NaOH)
Titration of 25.00 ml of 0.100 M HCl with 0.100 M NaOH

Titrations Involving a Strong Base and a Strong Acid

just the opposite of the case we have just discussed



Titration of 25.00 ml of 0.100 *M* HCl with 0.100 *M* NaOH

Titrations Involving a weak Acid and a Strong Base

Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 *M* NaOH after adding (a) 10.00 mL of 0.100 *M* NaOH, (b) 25.0 mL of 0.100 *M* NaOH, and (c) 35.0mL of 0.100 *M* NaOH.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 *M* NaOH after adding (a) 10.00 mL of 0.100 *M* NaOH.

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

2.5mmol	1.0mmol	0	0
1.5mmol	0	1.0mmol	1.0mmol

$$K_a = 1.8 \times 10^{-5}$$

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

1.5mmol	1.0mmol

Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 *M* NaOH after adding (a) 10.00 mL of 0.100 *M* NaOH.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$\frac{1.5\text{mmol}}{35.0\text{ mL}} = 4.28 \times 10^{-2}\text{ M} \qquad \frac{1.0\text{mmol}}{35.0\text{ mL}} = 2.8 \times 10^{-2}\text{ M}$$

$$K_a = \frac{[CH_3COO^-]\,[H^+]}{[CH_3COOH]} \qquad [H^+] = \frac{[CH_3COOH]\ K_a}{[CH_3COO^-]}$$

Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 *M* NaOH after adding (a) 10.00 mL of 0.100 *M* NaOH.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$[H^+] = \frac{(4.2 \times 10^{-2}\ M)(1.8 \times 10^{-5})}{2.8 \times 10^{-2}\ M} = 2.7 \times 10^{-5}$$

pH = 4.57

Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 *M* NaOH after adding (b) 25.0 mL of 0.100 *M* NaOH.

$$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$$

	2.5mmol	2.5mmol	0	0
	0	0	2.5mmol	2.5mmol

$$K_b = 5.6 \times 10^{-10}$$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$\frac{2.5\text{mmol}}{50.0\text{ mL}} = 5.0 \times 10^{-2}\text{ M}$$

Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 *M* NaOH after adding (b) 25.0 mL of 0.100 *M* NaOH.

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$5.0 \times 10^{-2}\ M - x$ | | x | x

$$5.6 \times 10^{-10} = \frac{x^2}{(5.0 \times 10^{-2} - x)}$$

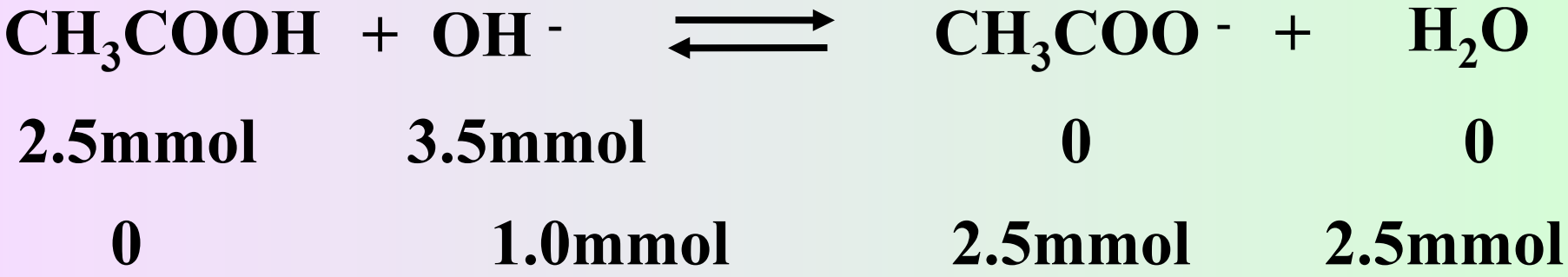
$$[OH^-] = x = 5.29 \times 10^{-6}$$

$$pOH = 5.27$$

$$pH = 8.72$$

Titrations Involving a weak Acid and a Strong Base

Calculate the pH in the titration of 25.0 mL of 0.100 M acetic acid with 0.100 *M* NaOH after adding (c) 35.0mL of 0.100 *M* NaOH.



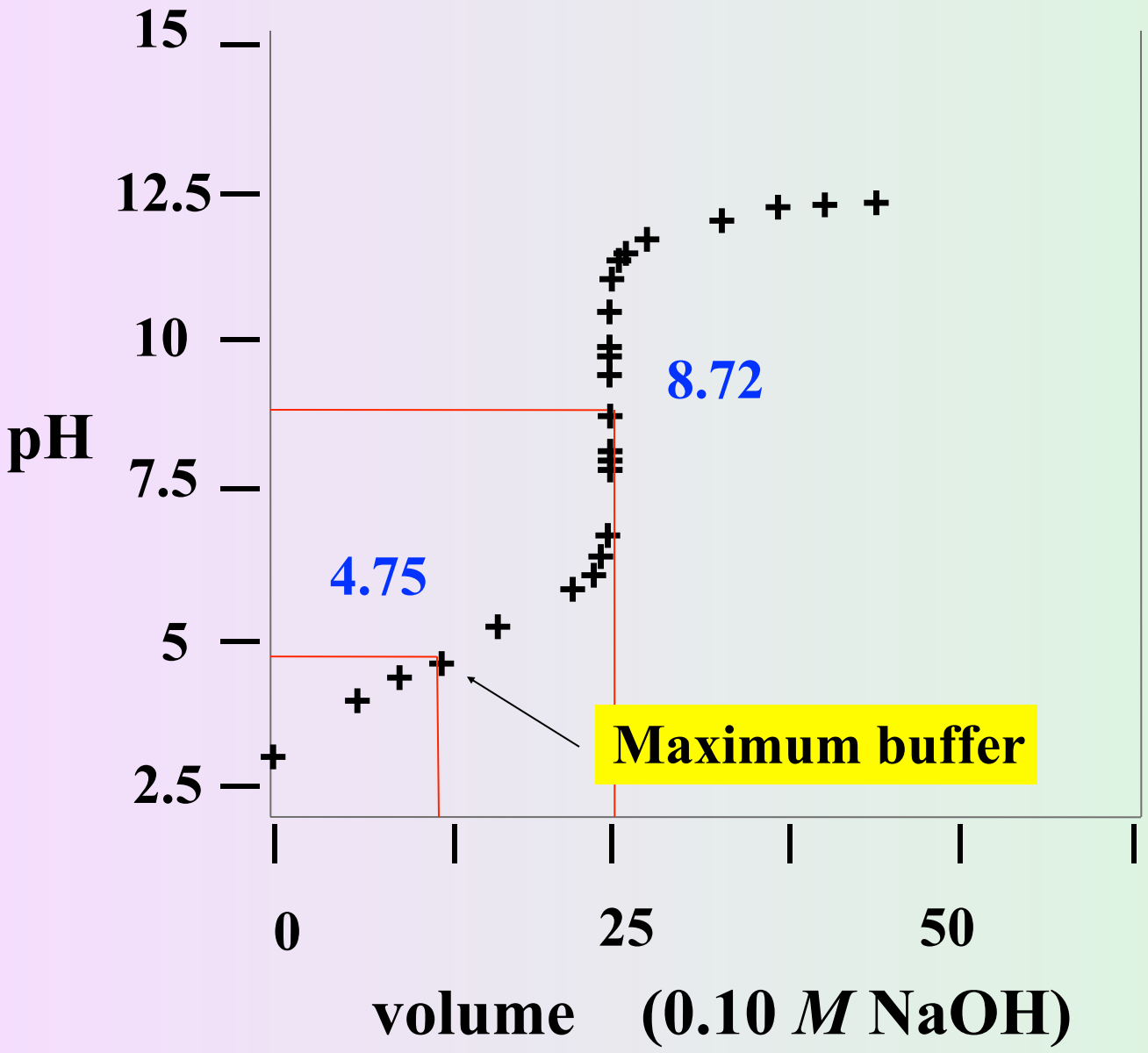
$$\frac{1.0\text{mmol } OH^-}{60.0\text{ mL (solution)}} = 1.67 \times 10^{-2}\text{ M}$$

pOH = 1.78

pH = 12.22

pH versus ml 0.10 M NaOH added

volume (NaOH)	volume (total)	mmol (HOAc)	mmol (NaOAc)	$[H^+]$	pH
0 ml	25.0ml	2.5	0	1.3×10^{-3}	2.87
10.0 ml	35.5 ml	1.5	1	2.7×10^{-5}	4.57
25.0 ml	50.0 ml	0	2.5	1.9×10^{-9}	8.72
			mmol (NaOH)	$[OH^-]$	
35.0 ml	60.0 ml	0	1	1.7×10^{-2}	12.22



Titration of 25.0 ml of 0.10 *M* acetic acid with 0.10 *M* NaOH

Titrations Involving a Strong Acid and a Weak Base

Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 *M* HCl with 0.100 *M* NH_3 after adding (a) 10.00 mL of 0.100 *M* NH_3, (b) 25.0 mL of 0.100 *M* NH_3, and (c) 35.0mL of 0.100 *M* NH_3.

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 *M* HCl with 0.100 *M* NH_3 after adding (a) 10.00 mL of 0.100 *M* NH_3.

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

2.5mmol	1.0mmol	0
1.5mmol	0	1.0mmol

$$[H^+] = \frac{1.5 \text{ mmol } H^+}{35.0 \text{ mL}} = 4.29 \times 10^{-2}$$

pH = 1.37

Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 *M* HCl with 0.100 *M* NH_3 after adding (b) 25.0 mL of 0.100 *M* NH_3.

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

2.5mmol	2.5 mmol	0
0	0	2.5 mmol

$$K_a = 5.6 \times 10^{-10}$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

$$\frac{2.5\text{mmol}}{50.0\text{ mL}} = 5.0 \times 10^{-2}\text{M}$$

Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 *M* HCl with 0.100 *M* NH_3 after adding (b) 25.0 mL of 0.100 *M* NH_3.

$$K_a = 5.6 \times 10^{-10}$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

$5.0 \times 10^{-2} - x$	x	x

$$5.6 \times 10^{-10} = \frac{x^2}{(5.0 \times 10^{-2} - x)}$$

$$[H^+] = x = 5.29 \times 10^{-6}$$

pH = 5.28

Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 *M* HCl with 0.100 *M* NH_3 after adding (c) 35.0mL of 0.100 *M* NH_3.

$$H^+ + NH_3 \rightleftharpoons NH_4^+$$

2.5mmol	3.5 mmol	0
0	1.0 mmol	2.5 mmol

$$K_a = 5.6 \times 10^{-10}$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

$$\frac{2.5\text{mmol}}{60.0\text{ mL}} = 4.1 \times 10^{-2}\text{M} \qquad \frac{1.0\text{mmol}}{60.0\text{ mL}} = 1.66 \times 10^{-2}\text{M}$$

Titrations Involving a Strong Acid and a Weak Base

Calculate the pH in the titration of 25.0 mL of 0.100 *M* HCl with 0.100 *M* NH_3 after adding (c) 35.0mL of 0.100 *M* NH_3.

$$K_a = 5.6 \times 10^{-10}$$

$$NH_4^+ \rightleftharpoons NH_3 + H^+$$

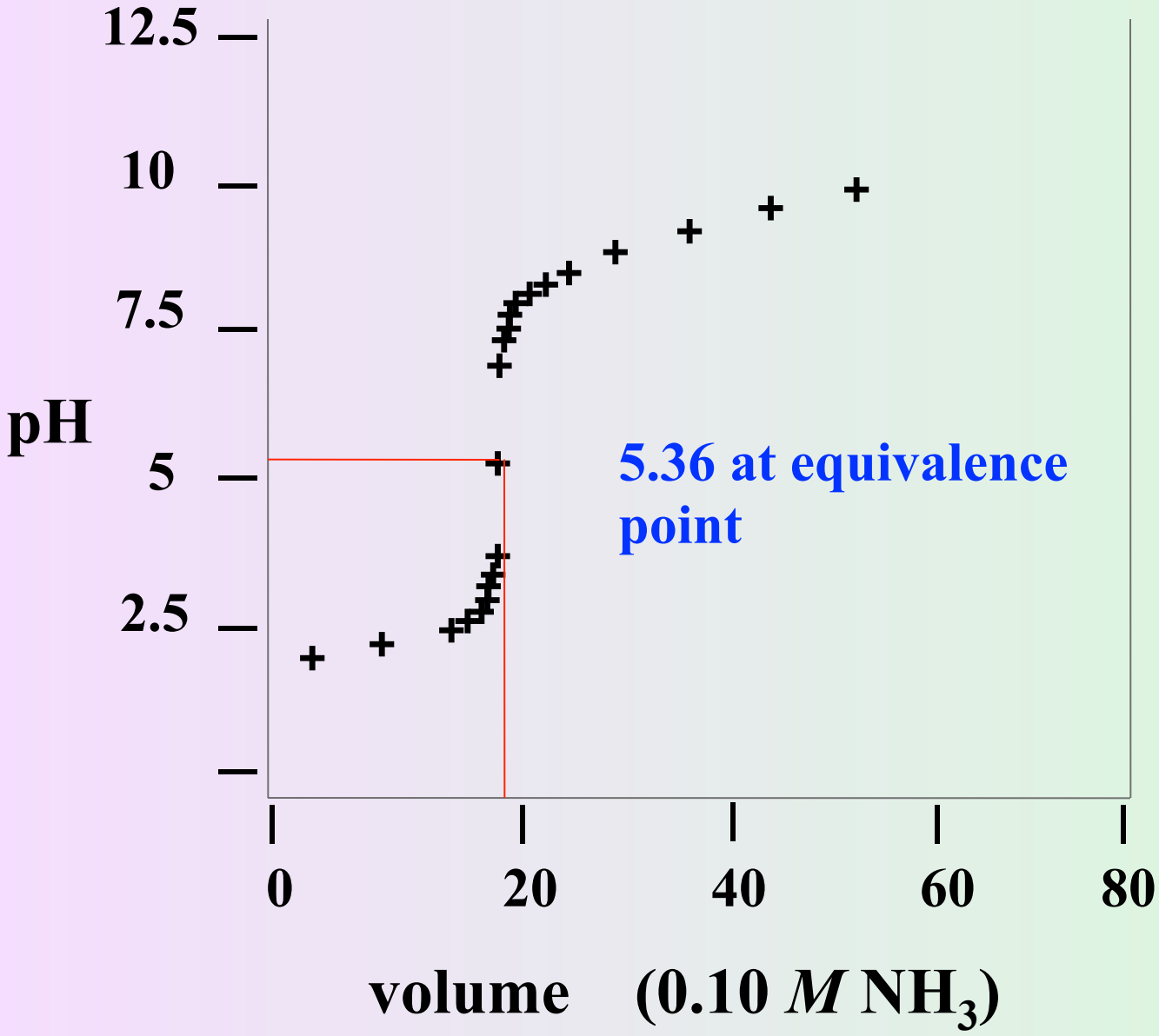
$$4.16 \times 10^{-2} \qquad 1.66 \times 10^{-2}$$

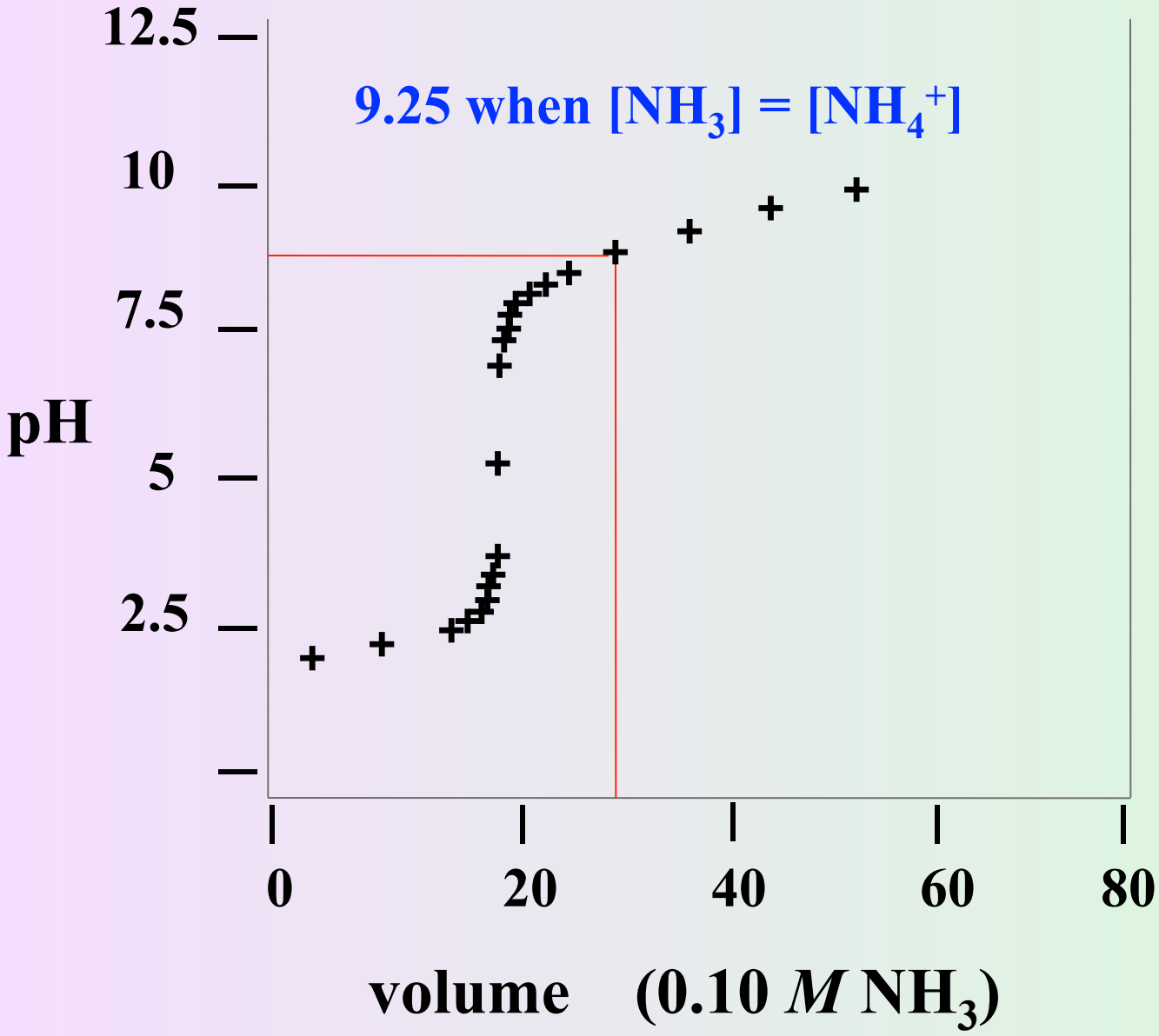
$$[H^+] = \frac{[NH_4^+]\ K_a}{[NH_3]} = \frac{(4.16 \times 10^{-2})(5.6 \times 10^{-10})}{1.66 \times 10^{-2}} = 1.4 \times 10^{-9}$$

pH = 8.85

pH versus ml 0.10 M NH_3 added

volume (NH_3)	volume (total)	mmol (HCl)	mmol (NH_4^+)	mmol (NH_3)	$[H^+]$	pH
0 ml	25.0ml	2.5			0.1	1.0
10.0 ml	35.0 ml	1.5			0.0429	1.37
25.0 ml	50.0 ml	2.5		0		5.28
35.0 ml	60.0 ml	2.5		1		8.85


12.5
10
7.5
pH
5
2.5
0
20
40
60
80
volume (0.10 M NH3)
5.36 at equivalence point
Titration of 25.0 ml of 0.10 M HCl acid with 0.10 M NH3



Titration of 25.0 ml of 0.10 *M* HCl acid with 0.10 *M* NH_3