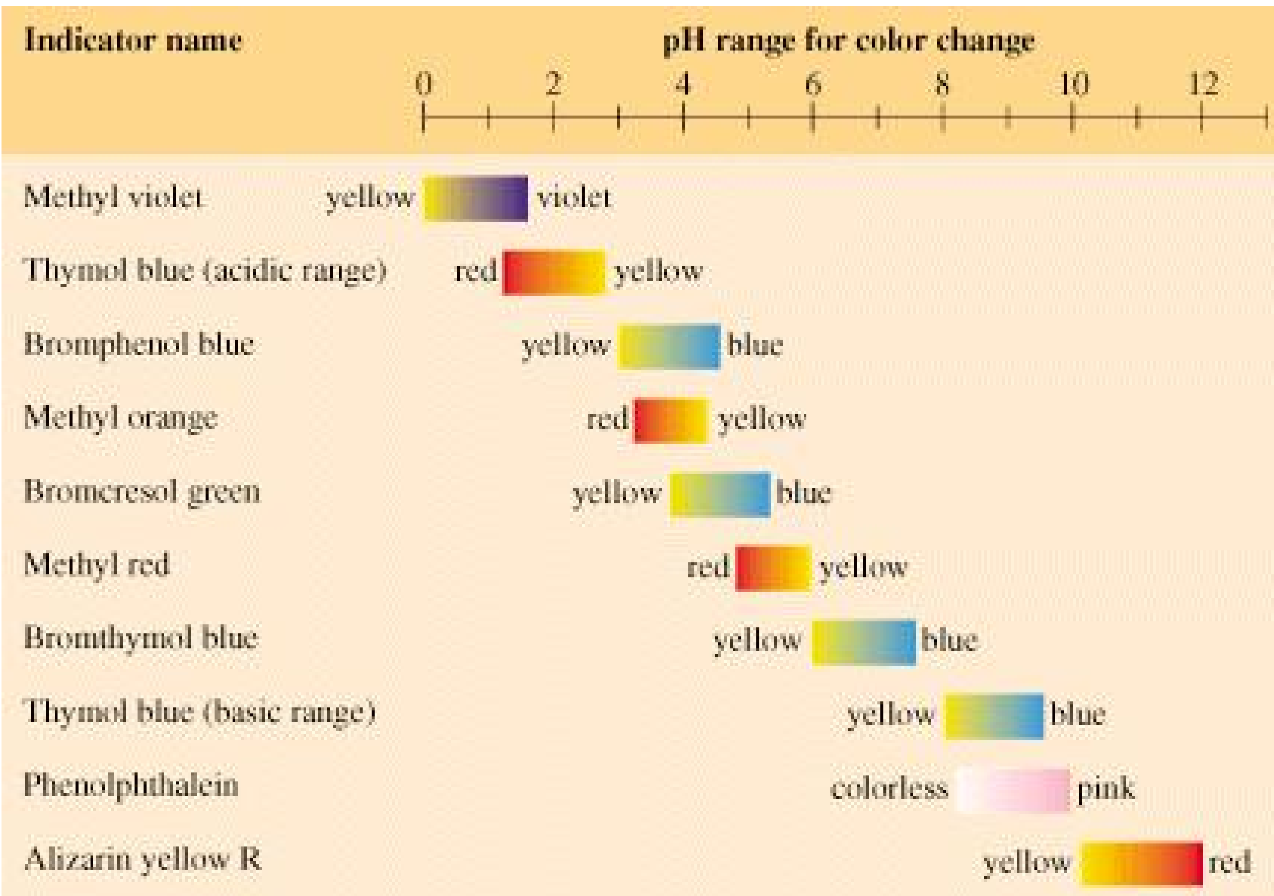
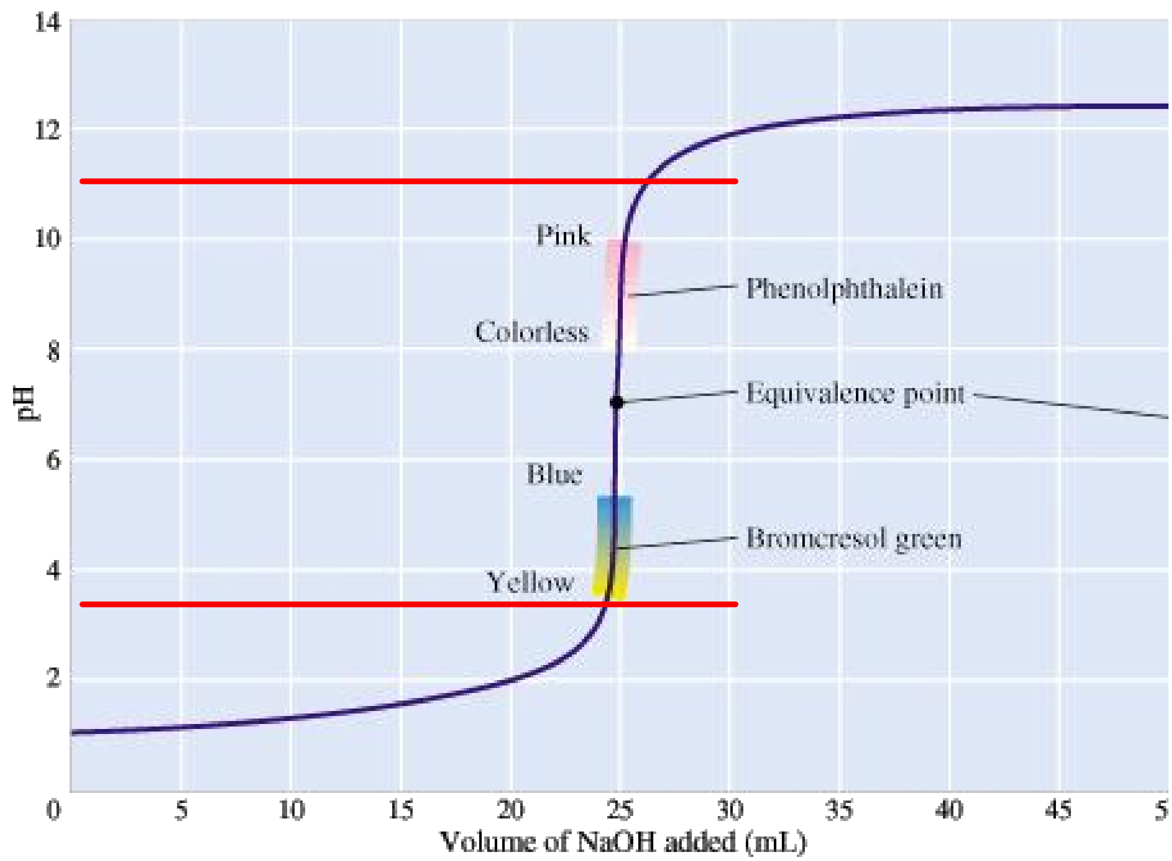
ACID–BASE TITRATION CURVES

- Titration is a procedure for determining the amount of acid (or base) in a solution by determining the volume of base (or acid) of known concentration that will completely react with it.
- Acid–base titration curve is a plot of the pH of a solution of acid (or base) against the volume of added base (or acid)
- These curves can be used to choose an indicator that will show when the titration is complete.



TITRATION OF A STRONG ACID BY A STRONG BASE

HCl (aq)	+	NaOH (aq)	—>	NaCl (aq)	+	H_2O (aq)
0.100 M		0.100 M				
25.00 mL		? mL				



First Part of Titration:
The pH changes slowly until about 24 mL of base is added (until the titration is near the equivalence point)

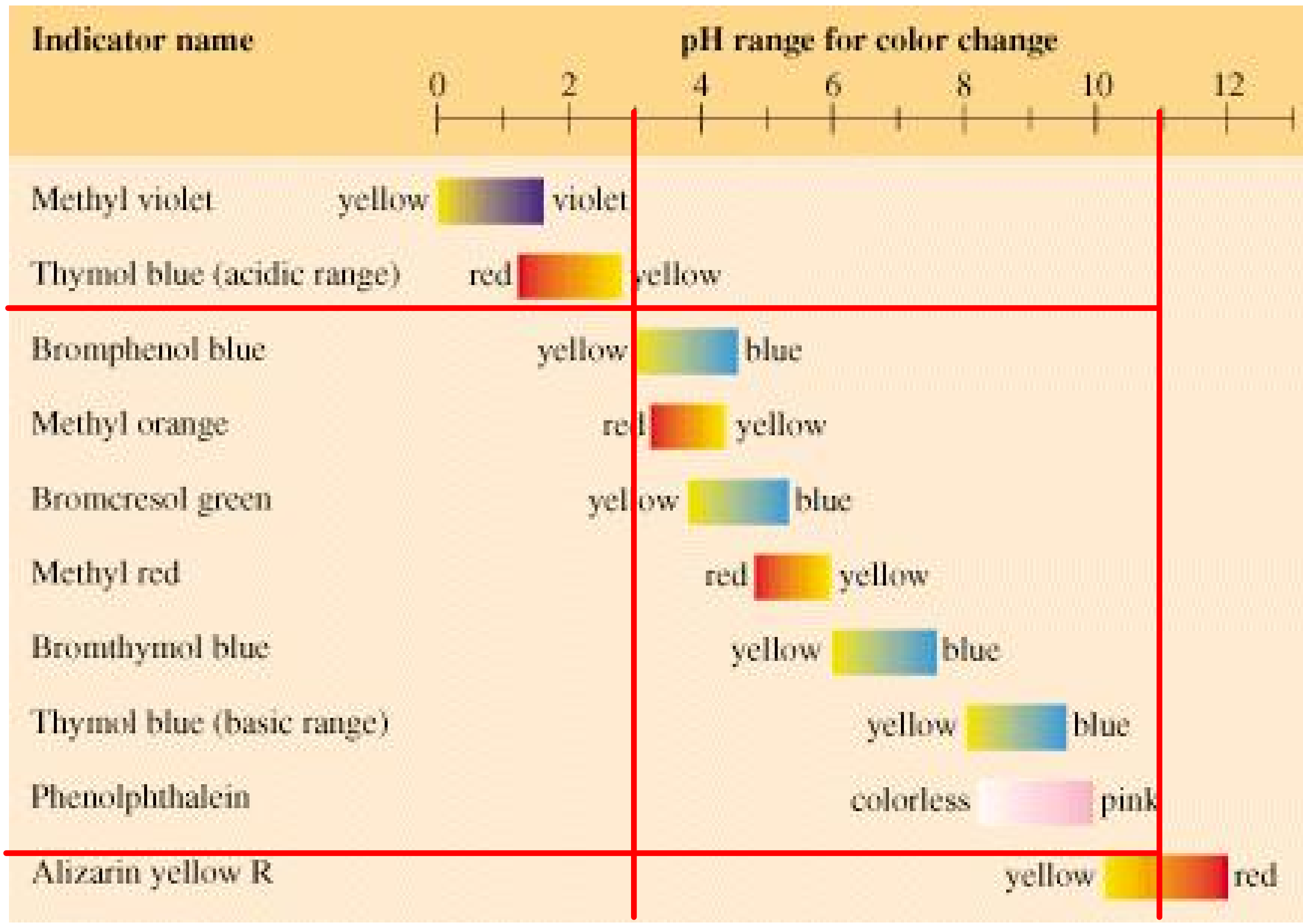
Second Part of Titration:
The pH changes rapidly from pH = 3 to pH = 11

At pH = 7:
- the solution contains NaCl, a salt that does not hydrolyze
- the equivalence point is reached

- **Equivalence point**: the point in a titration when a stoichiometric amount of reactant has been added

Choice of Indicator to detect equivalence point:

- The indicator should change color within the pH range **3 – 11**
- Which indicators change color within the **pH range of 3-11**?



CALCULATING THE PH OF A SOLUTION OF A STRONG ACID AND A STRONG BASE

Examples:

1. Calculate the pH of a solution in which 10.0 mL of 0.100 M HCl is added to 25.0 mL of 0.100 M NaOH.

HCl (aq)	+	NaOH (aq)	⟶	NaCl (aq)	+	H_2O (l)
strong acid		strong base				

	HCl +	NaOH ⟶	NaCl +	H_2O
Start	1.00 mmol	2.50 mmol	0	----
∆	–1.00 mmol	–1.00 mmol	+1.00 mmol	----
End	0	1.50 mmol	1.00 mmol	----

$$[OH^-] = \frac{1.50 \text{ mmoles}}{\text{Total Volume}} = \frac{1.50 \text{ mmoles } OH^-}{10.0 \text{ mL acid} + 25.0 \text{ mL base}} = \frac{1.50 \text{ mmoles } OH^-}{35.0 \text{ mL solution}}$$

$[OH^-] = 4.2\underline{8}6 \times 10^{-2}$ M   pOH = – log ($4.2\underline{8}6 \times 10^{-2}$) = 1.368

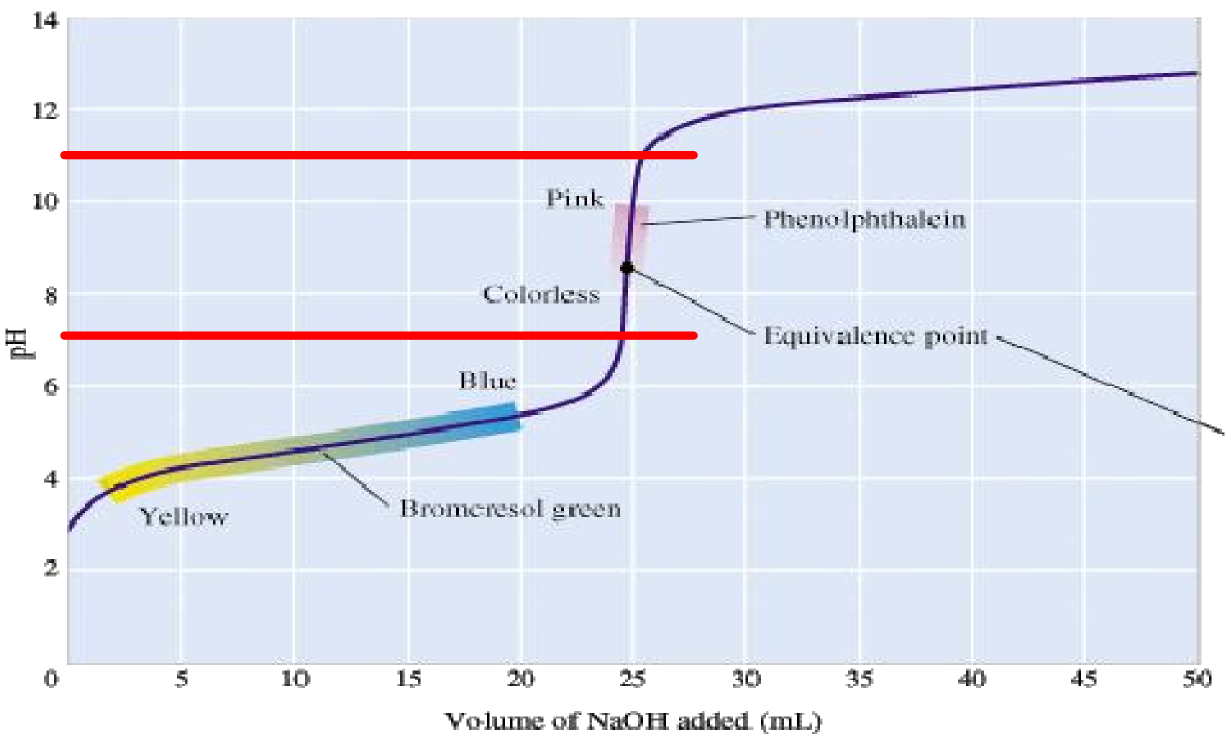
pH = 14.000 – 1.368 = **12.632**   **(strongly basic)**

2. Calculate the pH of a solution in which 30.0 mL of 0.100 M HCl is added to 25.0 mL of 0.100 NaOH.

TITRATION OF A WEAK ACID BY A STRONG BASE

$HC_2H_3O_2(aq)$ + $NaOH(aq)$ —> $NaC_2H_3O_2(aq)$ + $H_2O(aq)$

0.100 M 0.100 M
25.00 mL ? mL



First Part of Titration:
pH changes slowly at first (from about 3 to about 7)

NOTE:
- The titration starts at a higher pH (pH = 3) than HCl because $HC_2H_3O_2$ is a weak acid

Second Part of Titration:
pH changes rapidly from pH = 7 to pH = 11

NOTE:
- This is a shorter range than that for a strong acid by a a strong base (from 3 to 11)
- The equivalence point occurs on the basic side; this is the pH of the $NaC_2H_3O_2(aq)$

Choice of Indicator to detect equivalence point;

- The indicator should change color within the pH range **7 – 11**
- Which indicators change color within the **pH range of 7-11**?

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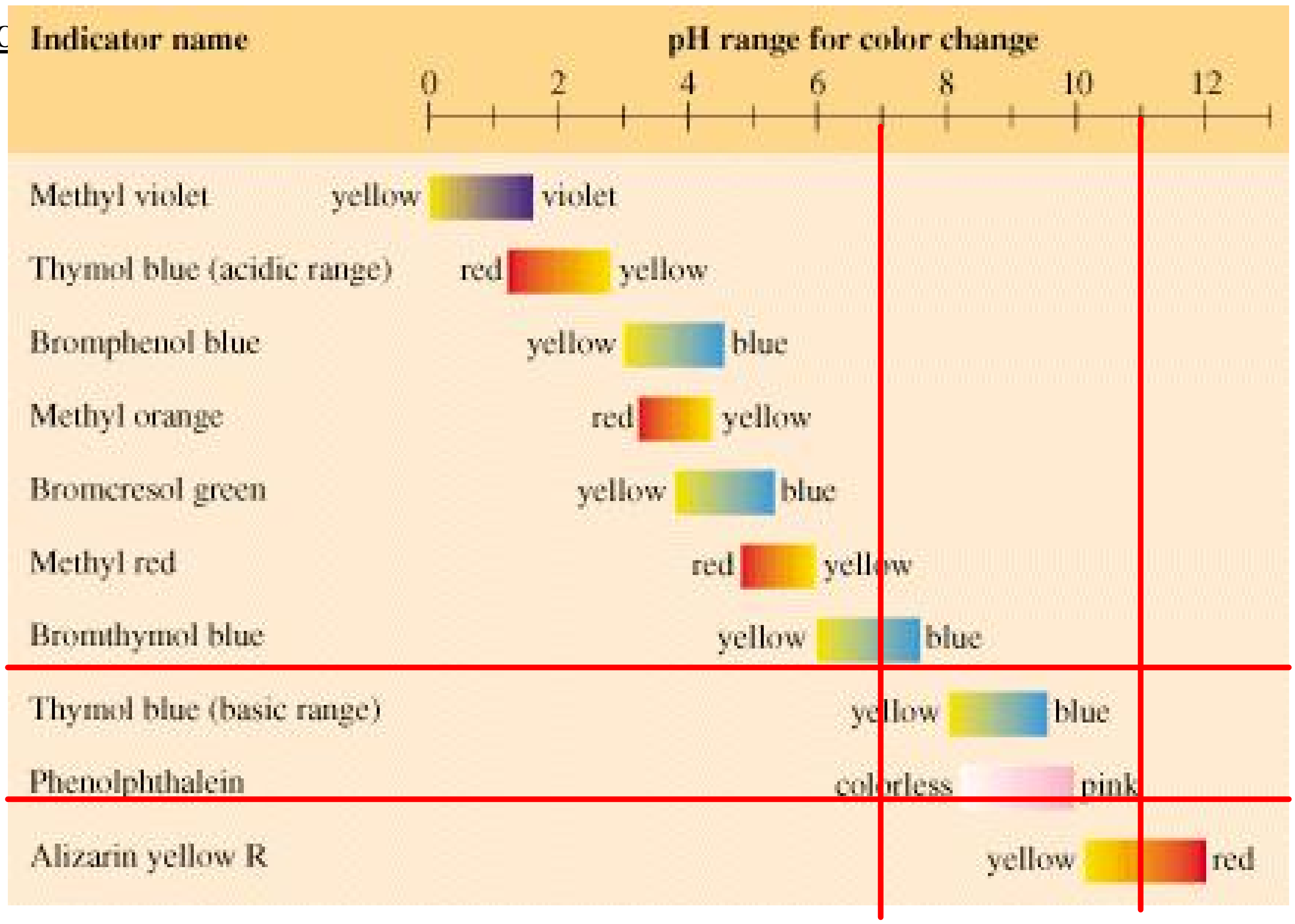


Calculating the pH at the Equivalence Point in the Titration of a Weak Acid by a Strong Base

Examples:

1. Calculate the pH at the equivalence point for the titration of 500. mL of 0.10 M acetic acid with 0.050 M sodium hydroxide. ($K_a = 1.7 \times 10^{-5}$)

First: Stoichiometry

$$HC_2H_3O_2(aq) + NaOH(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l)$$

At the equivalence point:
mmoles of $HC_2H_3O_2(aq)$ reacted = # mmoles of $NaOH(aq)$ reacted

$$HC_2H_3O_2\,(aq) + NaOH\,(aq) \longrightarrow NaC_2H_3O_2\,(aq) + H_2O\,(l)$$

$HC_2H_3O_2$ (aq)	NaOH (aq)
500. mL	? mL
0.10 M	0.050 M

$$?\text{mL NaOH} = 500.\text{ mL } HC_2H_3O_2 \times \frac{0.10\text{ moles } HC_2H_3O_2}{1\text{ L}} \times \frac{1\text{ mmol NaOH}}{1\text{ mmol } HC_2H_3O_2} \times \frac{1\text{ L NaOH}}{0.050\text{ mol NaOH}} = 1000\text{ mL}$$

$$HC_2H_3O_2\,(aq) + NaOH\,(aq) \longrightarrow NaC_2H_3O_2\,(aq) + H_2O\,(l)$$

$HC_2H_3O_2$ (aq)	NaOH (aq)
500. mL	1000 mL
0.10 M	0.050 M

	$HC_2H_3O_2$ +	NaOH $\longrightarrow$	$NaC_2H_3O_2$ +	H_2O
Start	50. mmol	50. mmol	0	----
Δ	–50. mmol	–50. mmol	+50. mmol	----
End	0	0 mmol	50. mmol	----

$$NaC_2H_3O_2(aq) \longrightarrow Na^+(aq) + C_2H_3O_2^-(aq)$$

Note: # mmoles $NaC_2H_3O_2$ = # mmoles $C_2H_3O_2^-$ = 50. mmol

$$[C_2H_3O_2^-] = \frac{50.\text{ mmol}}{\text{Total volume of solution}} = \frac{50.\text{ mmol}}{500.\text{ mL acid} + 1000\text{ mL base}} = 0.03\underline{3}3\text{ M}$$

Second: Hydrolysis of the acetate ion

$$\underset{\text{base}}{C_2H_3O_2^-(aq)} + H_2O \rightleftharpoons HC_2H_3O_2(aq) + OH^-(aq)$$

$K_b = ?$

Recall: $K_a(HC_2H_3O_2) \times K_b(C_2H_3O_2^-) = K_w$

$$K_b(C_2H_3O_2^-) = \frac{K_w}{K_a(HC_2H_3O_2)} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.\underline{88} \times 10^{-10}$$

	$C_2H_3O_2^-(aq)$ +	$H_2O(l)$ $\rightleftharpoons$	$HC_2H_3O_2(aq)$ +	$OH^-(aq)$
Initial	0.03$\underline{3}$3 M	----	0	0
Δ	–x	----	+x	+x
Equilibrium	0.03$\underline{3}$3–x	-----	x	x

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = \frac{x^2}{0.03\underline{3}3 - x} \approx \frac{x^2}{0.03\underline{3}3} = 5.\underline{88} \times 10^{-10}$$

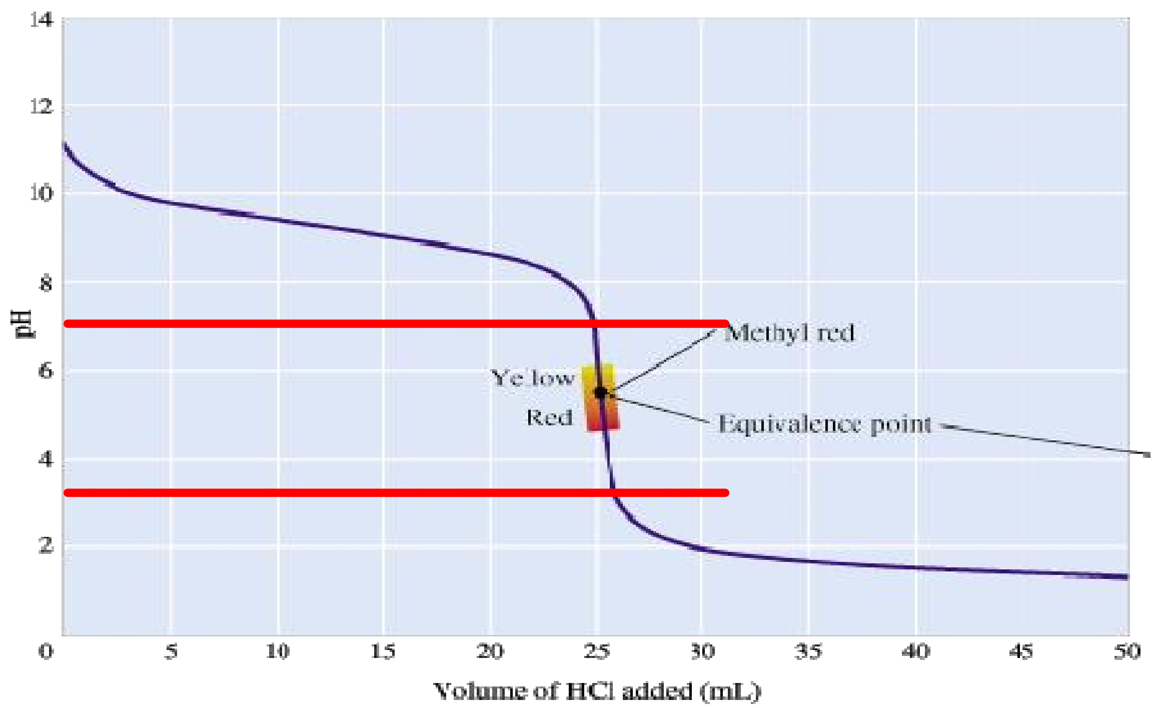
$x = [OH^-] = 4.43 \times 10^{-6}$ M $\qquad$ $pOH = -\log(4.43 \times 10^{-6}) = 5.35$

$pH = 14.00 - 5.35 = $ **8.65** **(basic, as expected)**

2. Calculate the pH at the equivalence point for the titration of 100. mL of 0.10 M acetic acid with 0.100 M sodium hydroxide. ($K_a = 1.7 \times 10^{-5}$)

TITRATION OF A WEAK BASE BY A STRONG ACID

NH_3	+	HCl(aq)	——>	NH_4Cl(aq)
0.100 M		0.100 M		
25.0 mL		?		



First Part of Titration:
pH changes slowly at first (from about 11 to about 7)

Second Part of Titration:
pH changes rapidly from pH = 7 to pH = 3

- This range of pH change (7 to 3) is about the same as that of a titration of a Weak Acid by a Strong Base (7 to 11)
- The equivalence point occurs on the acidic side; the pH at the equivalence point is the pH of NH_4Cl(aq)

Choice of Indicator to detect equivalence point

- The indicator should change color within the pH range **3-7**
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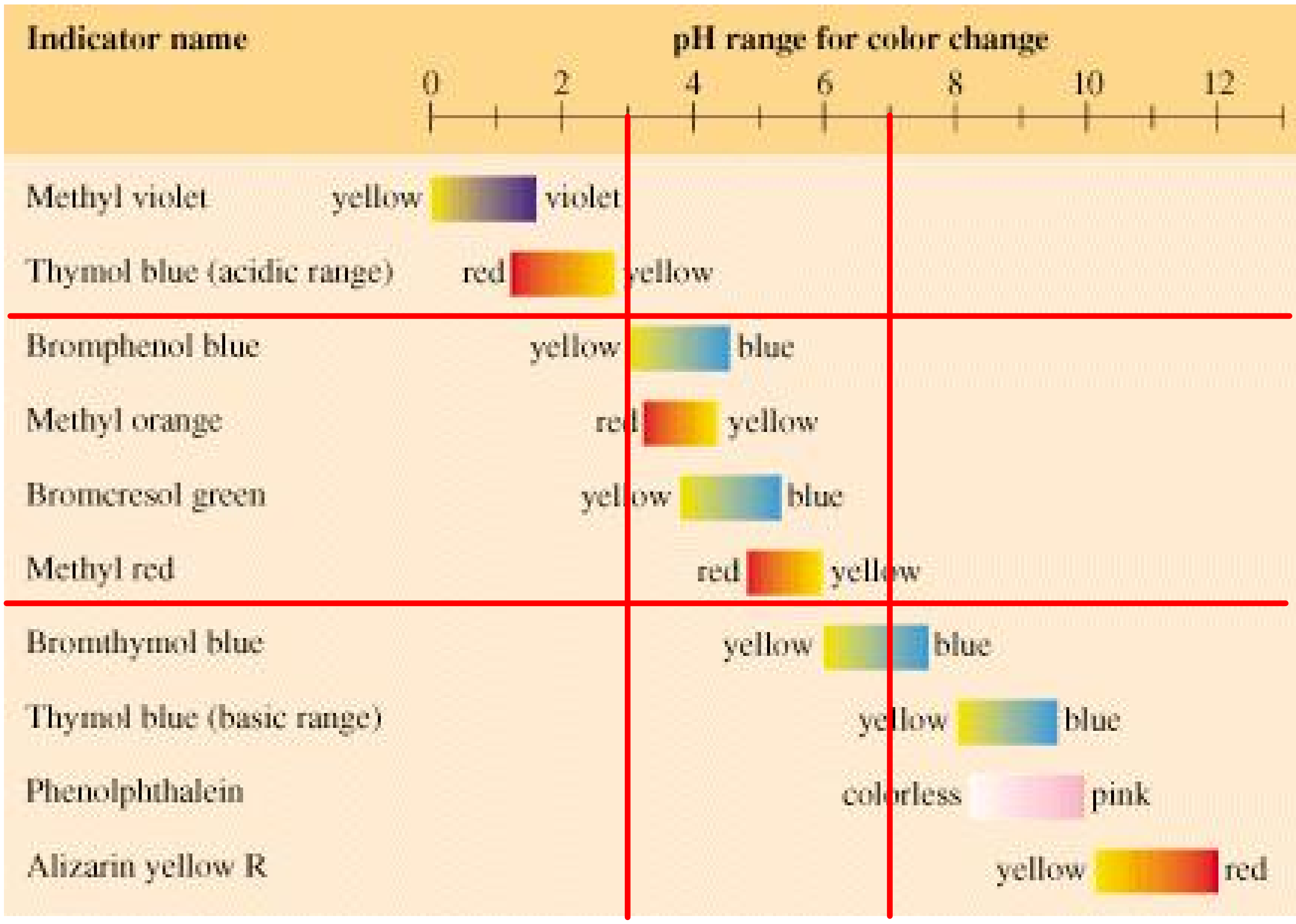
- Which indicators change color within the **pH range of 3-7** ?



Note:

- Because the range in which the rapid change of pH occurs is narrow (3 to 7), the choice of an indicator is more limited.

- The following indicators can be used:
  1. Bromphenol Blue
  2. Methyl Orange
  3. Bromcresol Green
  4. Methyl Red

CALCULATING THE PH AT THE EQUIVALENCE POINT IN THE TITRATION OF A WEAK BASE BY A STRONG ACID

Examples:

1. What is the pH at the equivalence point when 35 mL of 0.20 M ammonia is titrated by 0.12 M hydrochloric acid? (K_b for NH_3 is 1.8×10^{-5})

First: Stoichiometry

$HCl\,(aq) \quad + \quad NH_3\,(aq) \longrightarrow NH_4Cl\,(aq)$

At the equivalence point:
\# mmoles of NH_3 reacted = # mmoles of HCl reacted

$HCl\,(aq) \quad + \quad NH_3\,(aq) \longrightarrow NH_4Cl\,(aq)$

? mL 35 mL
0.12 M 0.20 M

$$? \text{ mL} = 35 \text{ mL } NH_3 \times \frac{0.20 \text{ mmol } NH_3}{1 \text{ mL}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol } NH_3} \times \frac{1 \text{ mL HCl}}{0.12 \text{ mmol HCl}} = 5\underline{8}.3 \text{ mL HCl}$$

$HCl\,(aq) \quad + \quad NH_3\,(aq) \longrightarrow NH_4Cl\,(aq)$

$5\underline{8}.3$ mL 35 mL
0.12 M 0.20 M

	HCl +	NH₃ ⟶	NH₄Cl
Start	70. mmol	70. mmol	0
Δ	–70. mmol	–70. mmol	+70. mmol
End	0	0 mmol	70. mmol

$NH_4Cl\,(aq) \longrightarrow NH_4^+\,(aq) \quad + \quad Cl^-\,(aq)$

Note: # mmoles NH_4Cl = # mmoles NH_4^+ = 70. mmol

$$[NH_4^+] = \frac{70. \text{ mmol}}{\text{Total Volume of Solution}} = \frac{70. \text{ mmol}}{35 \text{ mL base} + 5\underline{8}.3 \text{ mL acid}} = 0.075 \text{ M}$$

Second: Hydrolysis of the ammonium ion

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq)$$

acid

$K_a(NH_4^+) = ?$

Recall: $K_a(NH_4^+) \times K_b(NH_3) = K_w$

$$K_a(NH_4^+) = \frac{K_w}{K_b(NH_3)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.\underline{5}6 \times 10^{-10}$$

	NH_4^+ (aq)	+ H_2O (l) ⇌	NH_3 (aq)	+ OH^- (aq)
Initial	0.075 M	----	0	0
Δ	–x	----	+x	+x
Equilibrium	0.075–x	-----	x	x

$$K_a = \frac{[NH_3]\,[H_3O^+]}{[NH_4^+]} = \frac{x^2}{0.075 - x} \approx \frac{x^2}{0.075} = 5.\underline{5}6 \times 10^{-10}$$

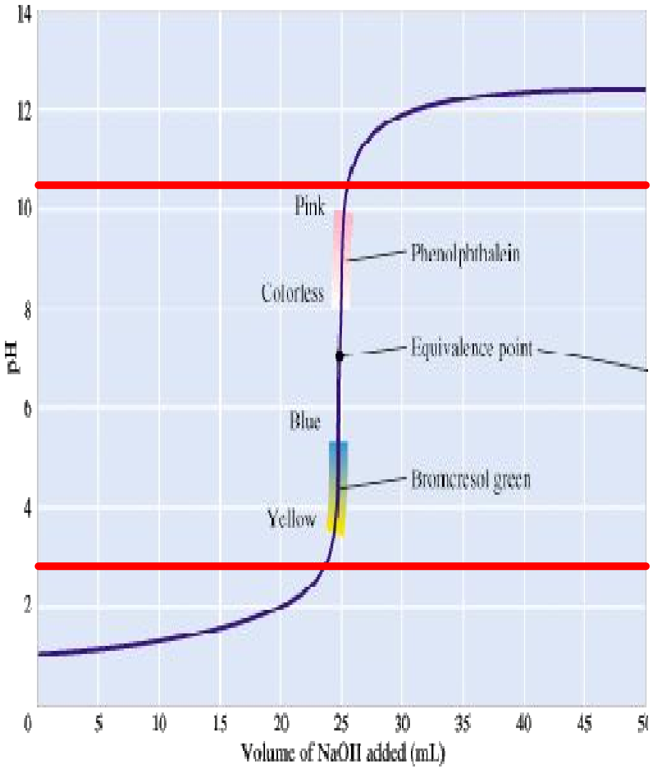
$x = [H_3O^+] = 6.\underline{4}6 \times 10^{-6}$ $pH = -\log(6.\underline{4}6 \times 10^{-6}) =$ **5.19** **(acidic, as expected)**

2. What is the pH at the equivalence point when 50 mL of 0.10 M ammonia is titrated by 0.25 M hydrochloric acid ? (K_b for NH_3 is 1.8×10^{-5})

ACID-BASE TITRATIONS (SUMMARY)

Strong Acid by A Strong Base

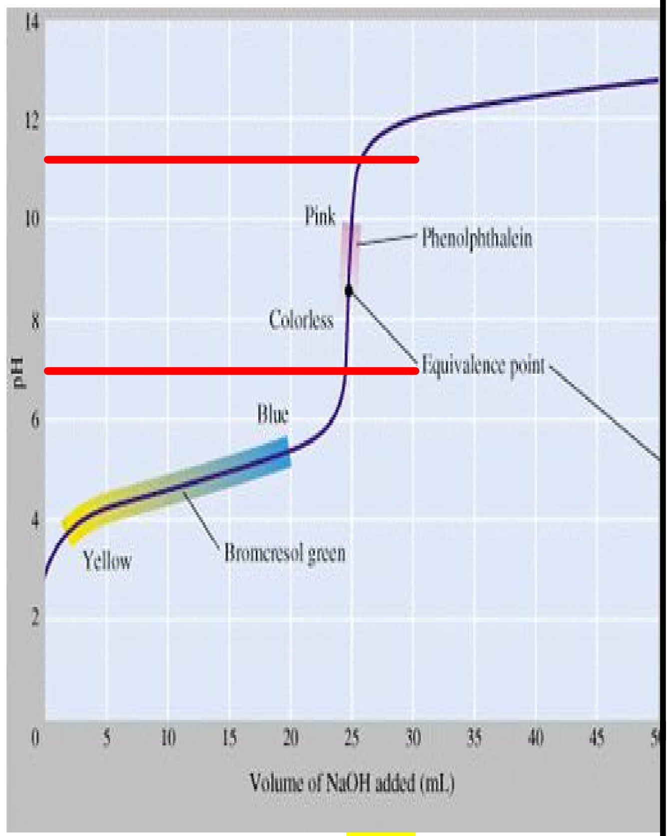
HCl (aq) + NaOH (aq) ⟶ **NaCl(aq)**



Solution is neutral at
Equivalence Point
(Rapid Change of pH =3-11)

Weak Acid by A Strong Base

$HC_2H_3O_2$ (aq) + NaOH (aq) ⟶ **$NaC_2H_3O_2$(aq)**



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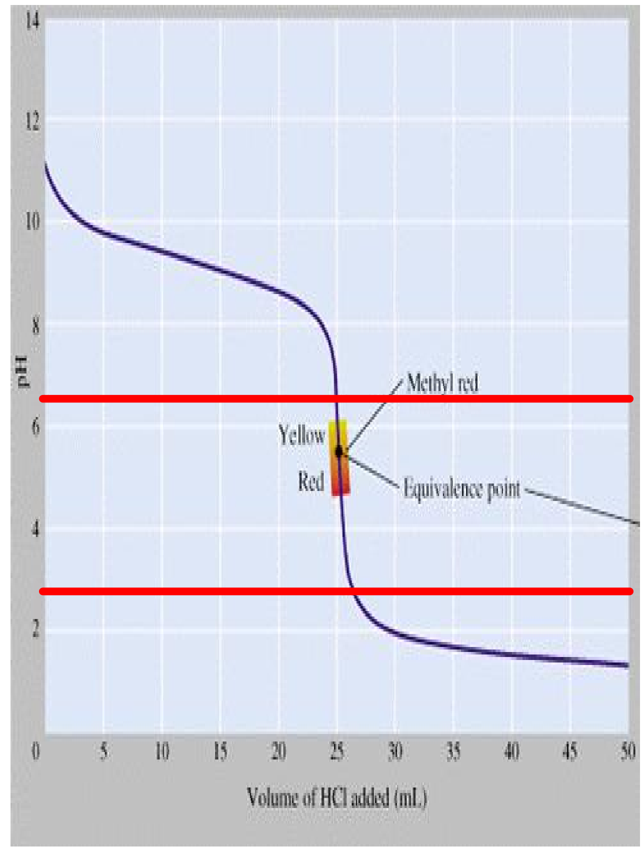
Solution is **basic** at
Equivalence Point
Rapid Change of pH =7-11

Weak Base by a Strong Acid

NH_3 (aq) + HCl (aq) ⟶ **NH_4Cl(aq)**



Solution is **acidic** at
Equivalence Point
Rapid Change of pH=3-7