Chapter 18: Aqueous Ionic Equilibria II

Acid-base titrations

Chem 102
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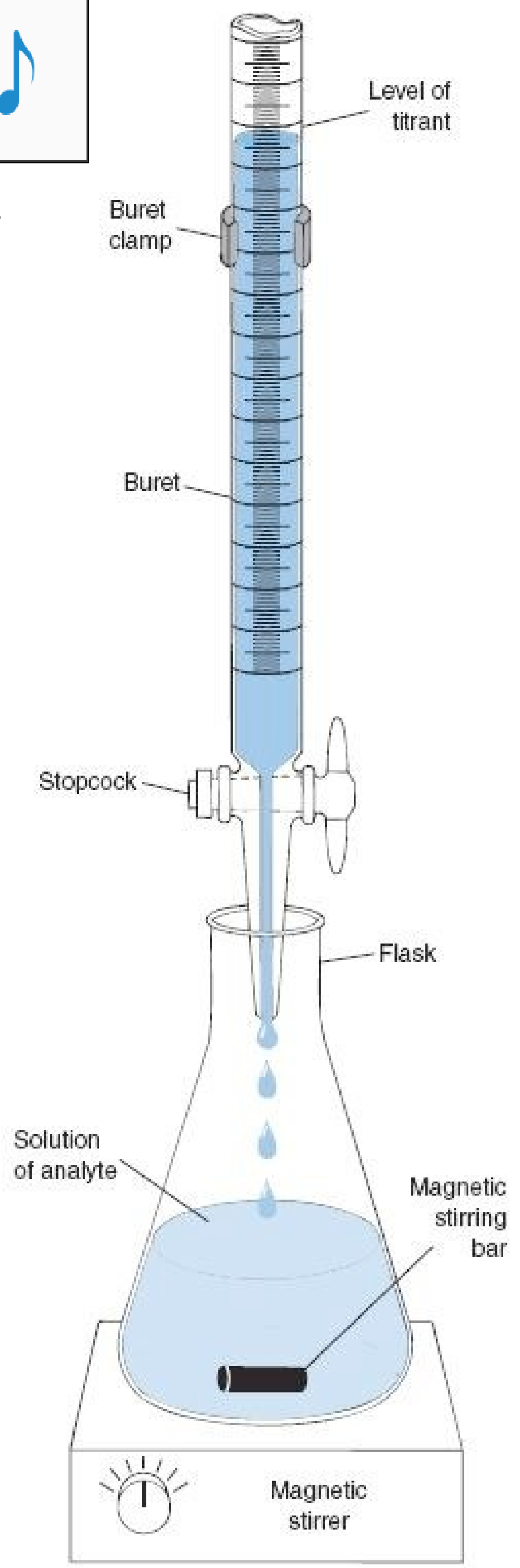
Acid-Base titrations

- In an acid-base **titration**, an acid (or base) of known quantity and concentration is reacted with a base (or acid) of unknown concentration
- The **endpoint** or **equivalence point** is reached when an added indicator just changes color
- Care must be taken not to exceed the endpoint where the acid is **exactly neutralized** by the base.
- Usually the amount of (known concentration) **titrant** added to the solution is used to determine the (unknown) concentration of the solution.
- The titrant is usually in the burette.



Acid-Base titrations

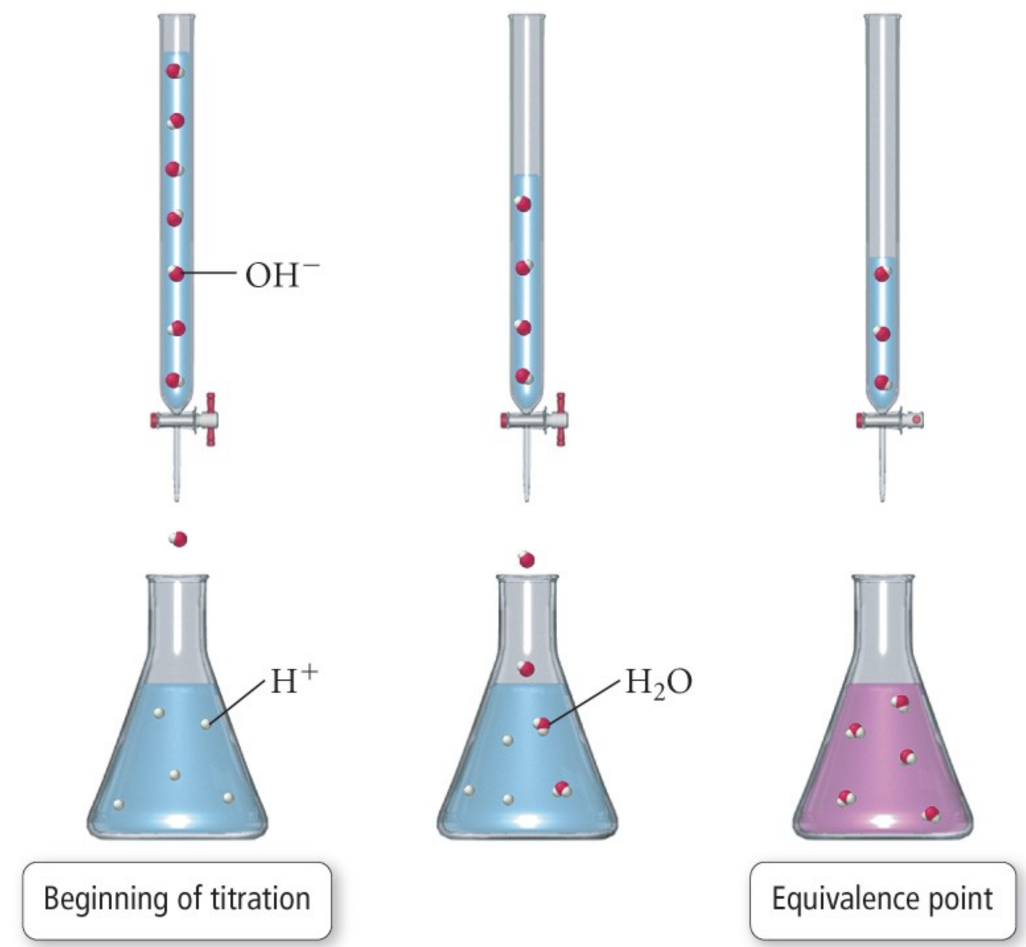
- At the endpoint, enough titrant has been added to exactly **neutralize** the solution:

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

- At the endpoint the *added* H^+ and OH^- moles are equal.

- Note that the endpoint pH is not necessarily 7!

Indicator changes color



Titration calculations

moles ⟺ moles

- Relate moles to moles because the volume is changing!
- An indicator or measurement of pH will allow you to determine the **equivalence point:**

  the point in the titration when added

  moles of acid = moles of base

  where neither acid nor base are in excess
- Determine the concentration of the unknown acid or base:

$$M_1V_1 = M_2V_2 \longleftrightarrow \left(\frac{mol}{L}\right)(L) = \left(\frac{mol}{L}\right)(L) \longleftrightarrow mol = mol$$

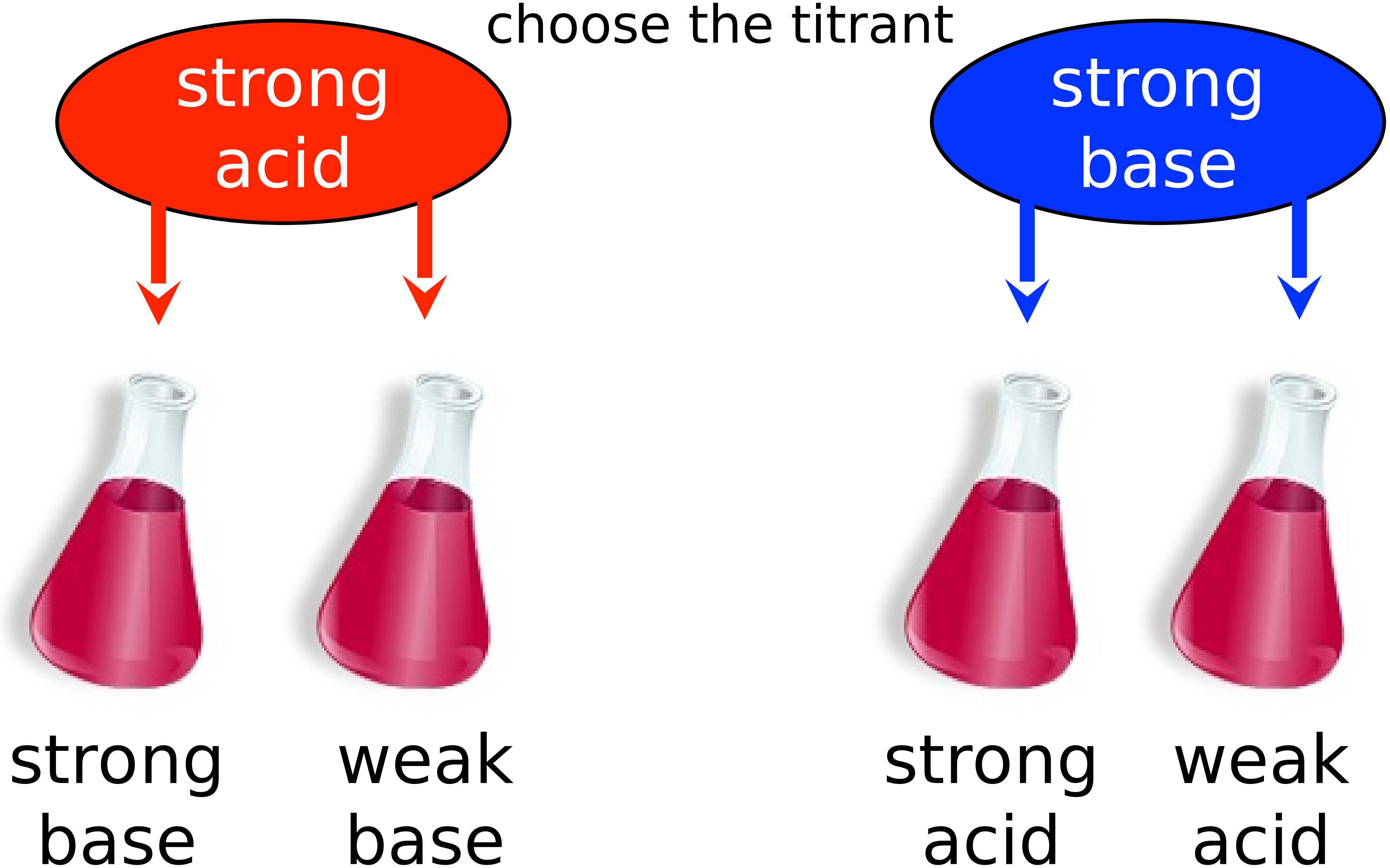
Types of Acid-Base titrations

Titrant should be chosen either a strong acid or a strong base:

1. Strong Acid with Strong Base
2. Strong Base with Strong Acid
3. Weak Acid with Strong Base
4. Weak Base with Strong Acid

Four types of acid-base titrations

We can always choose the titrant

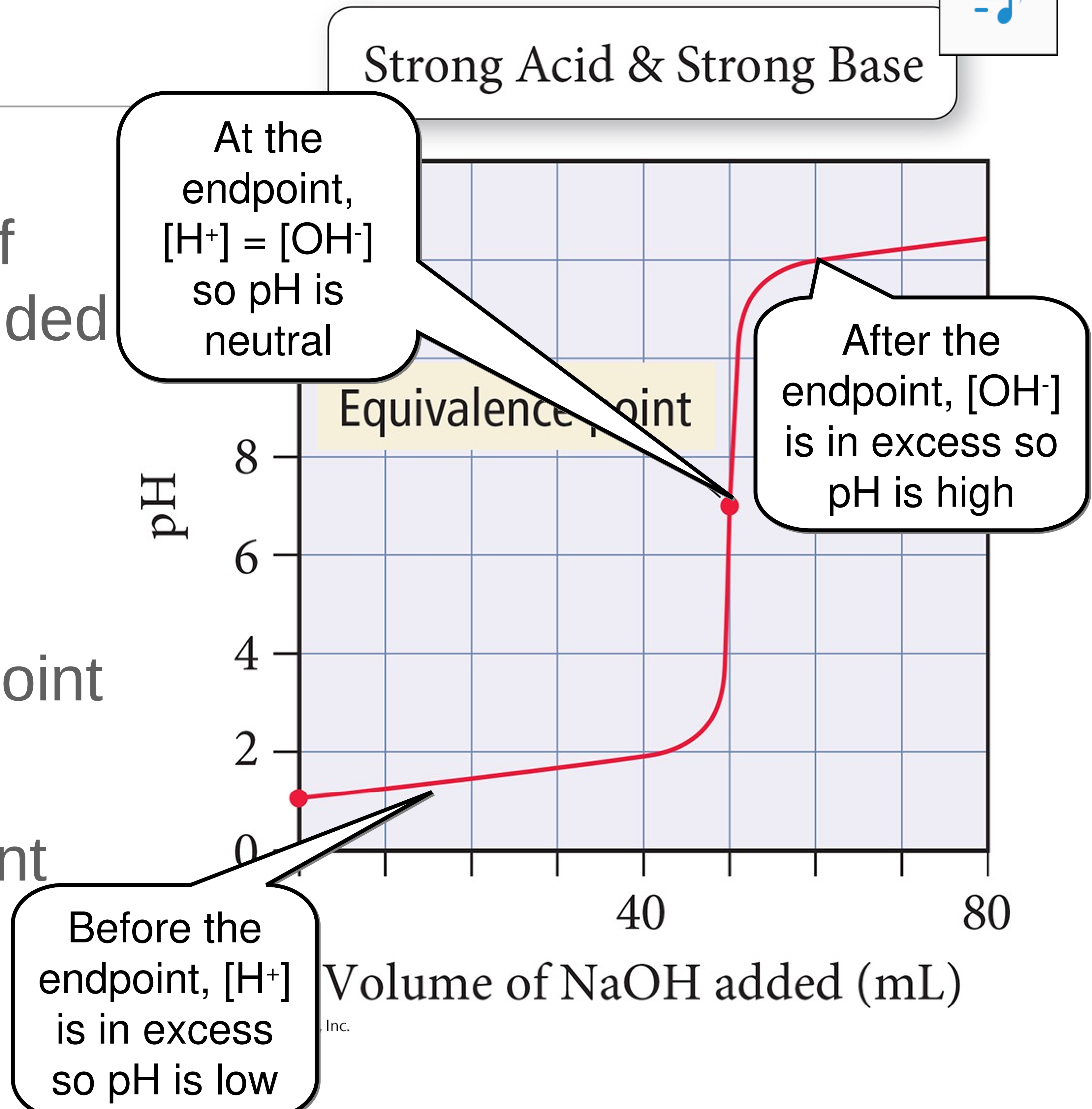


Titration Curves

- Plot pH as a function of the volume of titrant added

- Break into regions:

  - **before** equivalence point
  - **at** equivalence point
  - **after** equivalence point



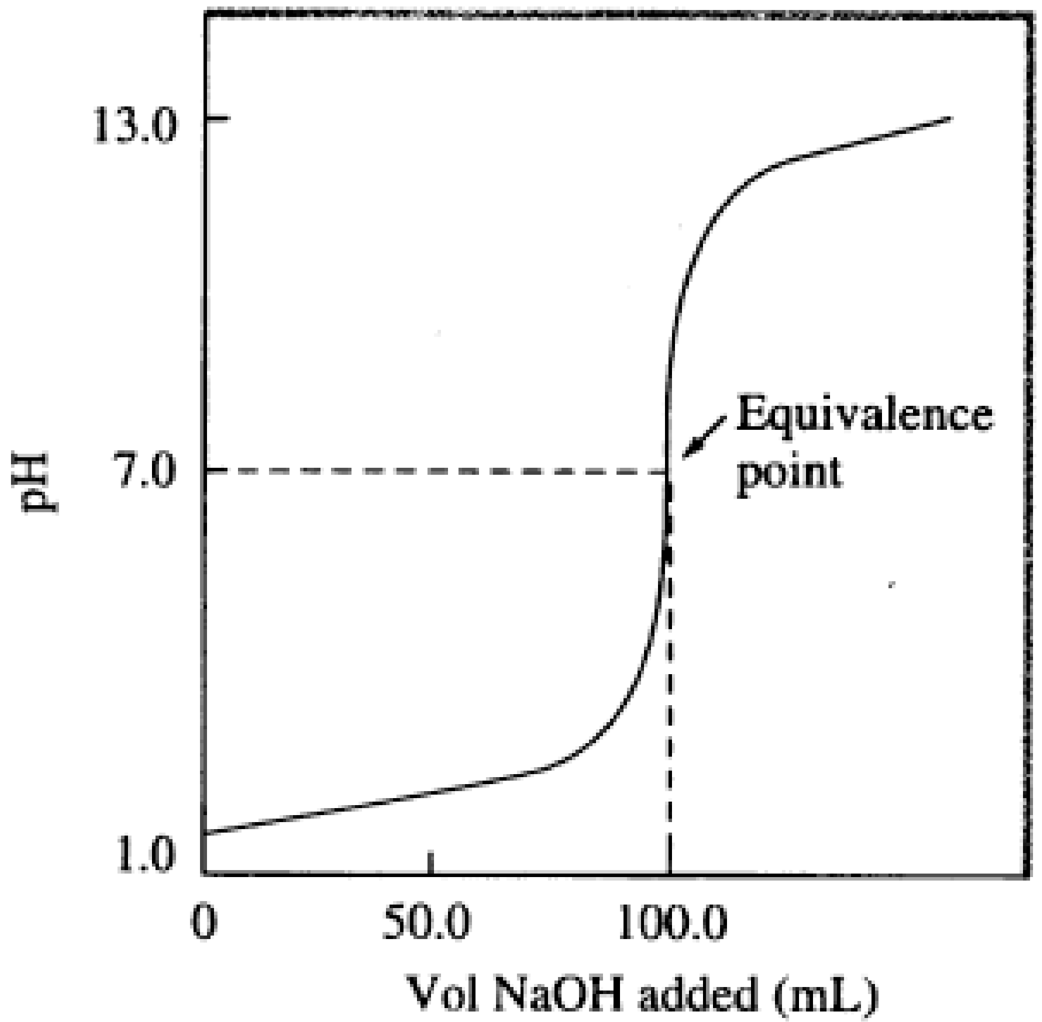
Titration of strong acid with strong base

Example. Consider titration of 50.0 mL of 0.200 M HNO_3 (strong acid) with 0.100 M NaOH (strong base).

titrant (in buret)

Overview:

- Net reaction: $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$
- Equivalence point pH = 7 (*only for strong acid – strong base*)
- Very large change in pH near the equivalence point
- Before equivalence point the pH depends on excess of strong acid
- After equivalence point the pH depends on excess of strong base



Titration of strong acid with strong base

1. Equivalence point

NaOH neutralizes all HNO_3:

$$moles\ acid = moles\ base$$

$$Initial\ moles\ HNO_3\ = (0.200\ mol/L)(0.0500\ L) = 0.01\ moles$$

Therefore 0.01 mol of NaOH needed to neutralize.

$$(0.0100\ mol\ NaOH)(\frac{1\ L}{0.100\ mol}) = 0.100\ L = 100\ mL$$

of NaOH

Alternatively, you could use this formula directly:

$$M_aV_a = M_bV_b$$

$$V_b = \frac{M_aV_a}{M_b} = \frac{(0.200\ M)(50.0\ mL)}{0.100\ M} = 100\ mL\ NaOH$$

Titration of strong acid with strong base

2. Initial pH before adding any NaOH:

$pH = -\log([H^+]) = -\log(0.200\ M) = 0.70$

Remember that HNO_3 is a strong acid and dissociates fully in water.

Titration of strong acid with strong base

3. pH after adding 25.0 mL of NaOH

Moles of NaOH added = moles of OH^- added = (0.0250 L)(0.100 mol/L) = 0.0025 mol.

(moles)	$H_3O^+(aq)$	+	$OH^-(aq)$	→	$2\ H_2O(l)$
Before	0.010		--		--
Addition	--		0.0025		--
After	0.010-0.0025 = 0.008		0		--

Titration of strong acid with strong base

So, 0.008 moles of H_3O^+ remain in the solution.

New volume = 50.0 mL + 25.0 mL = 75.0 mL.

$[H_3O^+]$ = 0.008 mol / 0.0750 L = 0.1 M

and therefore pH = 1.0.

This is larger than the initial pH 0.70, which is expected as we are adding base.

Titration of strong acid with strong base

4. pH after adding total of 50.0 mL NaOH

Moles of NaOH added = (0.0500 L)(0.100 mol/L) = 0.005 moles of OH^- added.

So, 0.010 – 0.005 = 0.005 moles of H_3O^+ remain after neutralization.

New volume = 50.0 mL + 50.0 mL = 100.0 mL.

$[H_3O^+]$ = 0.0050 mol / 0.100 L = 0.05 M

and hence pH = 1.30 (increases).

Titration of strong acid with strong base

5. pH after adding total of 75.0 mL NaOH

Moles of NaOH added = (0.0750 L)(0.100 mol/L) = 0.0075 moles OH^- of added.

So, 0.010 – 0.0075 = 0.0025 moles of H_3O^+ remain after neutralization.

New volume = 50.0 mL + 75.0 mL = 125.0 mL.

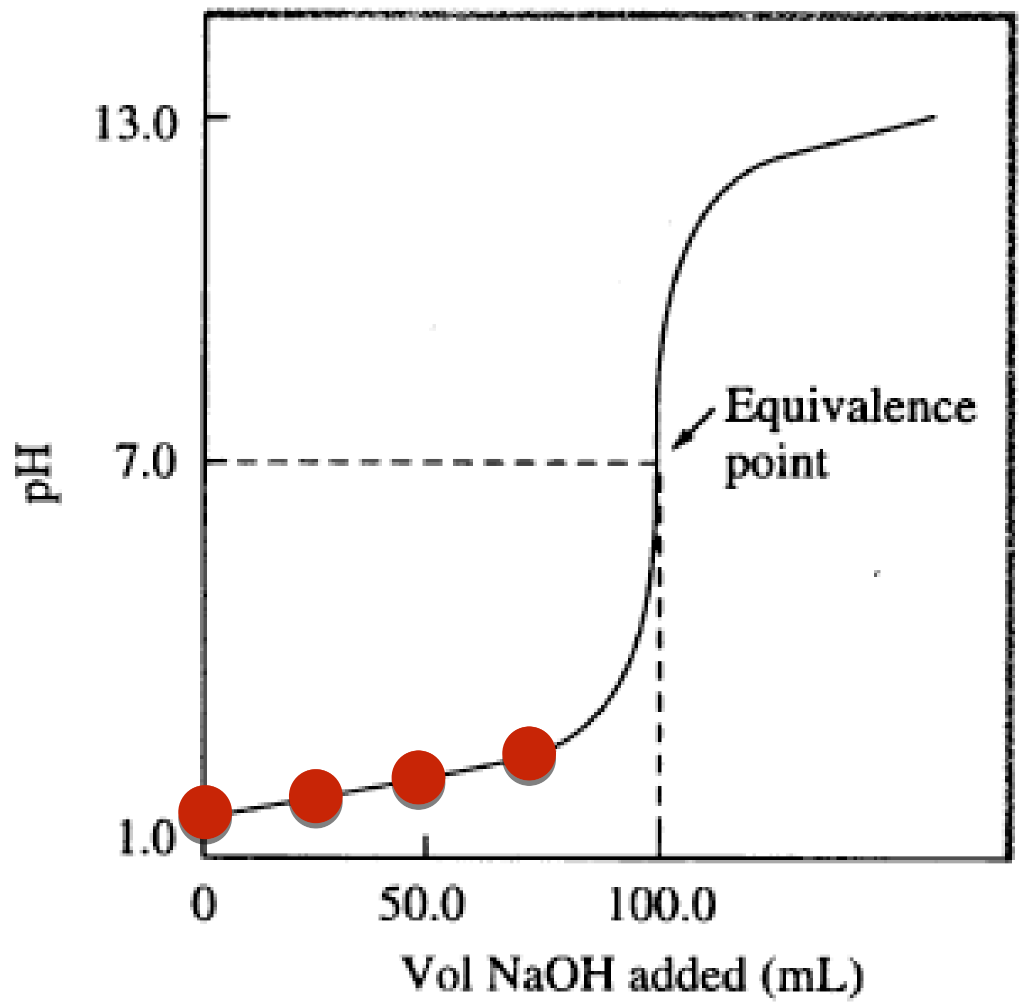
$[H_3O^+]$ = 0.0025 mol / 0.125 L = 0.02 M

and hence pH = 1.70 (increases).

Titration of strong acid with strong base

Summary so far:

Vol NaOH added (mL)	pH
0.00	0.70
25.0	1.00
50.0	1.30
75.0	1.70



Titration of strong acid with strong base

6. pH after adding 100.0 mL of NaOH (equiv. Point)

Moles of NaOH added = (0.100 L)(0.100 mol/L) = 0.010 moles of OH^- added.

So, 0.010 – 0.010 = 0.000 moles of H_3O^+ remain (all neutralized).

New volume = 50.0 mL + 100.0 mL = 150.0 mL.

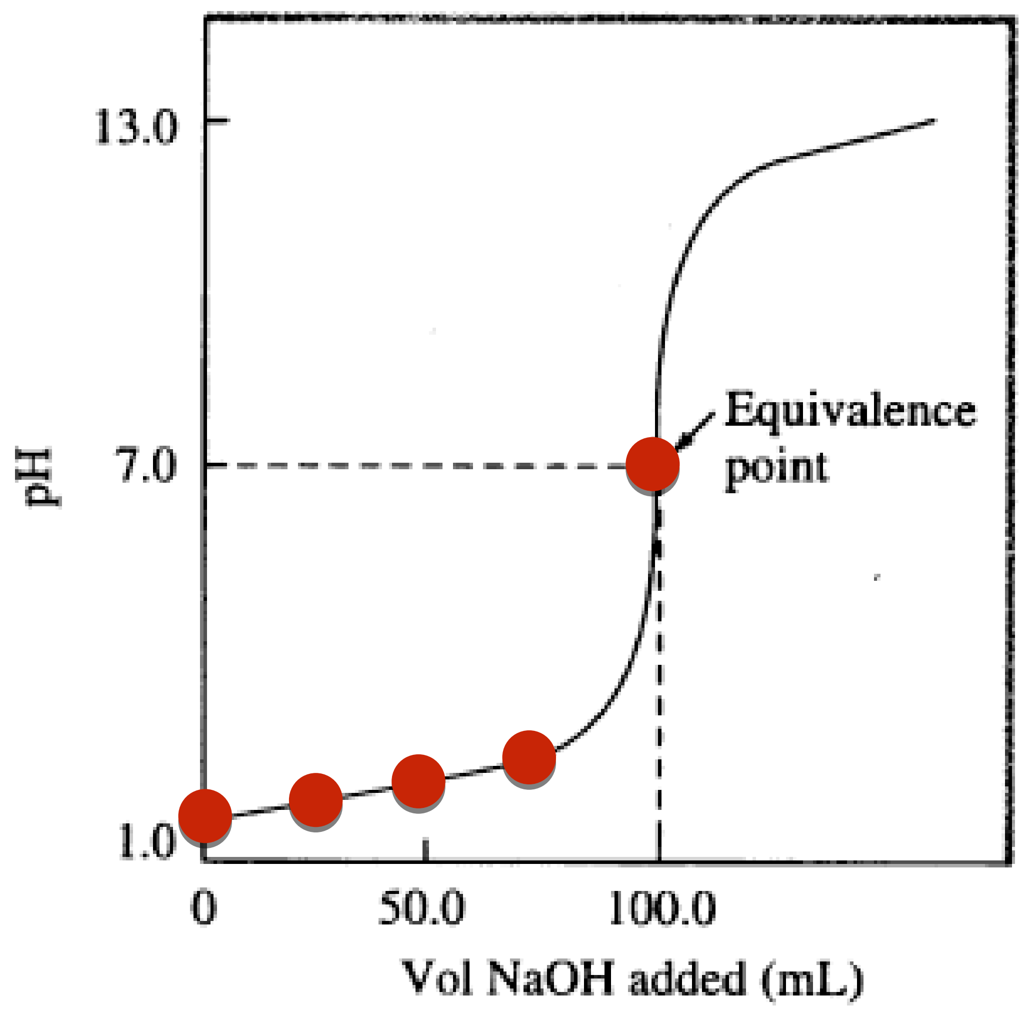
$[H_3O^+] = 1.0 \times 10^{-7}$ M (from autoionization).

pH = 7 (only neutral for strong acid – strong base titration).

Titration of strong acid with strong base

Summary so far:

Vol NaOH added (mL)	pH
0.00	0.70
25.0	1.00
50.0	1.30
75.0	1.70
100.0	7.00



pH = 7.00 at the equivalence point for a strong acid-strong base titration

Titration of strong acid with strong base

7. pH after adding 125.0 mL of NaOH

Moles of NaOH added = (0.1250 L)(0.100 mol/L) = 0.0125 moles of OH^- added.

Only 0.0100 moles of H_3O^+ to start, so we have an **excess** of OH^- of 0.0025 mol.

New volume = 50.0 mL + 125.0 mL = 175.0 mL.

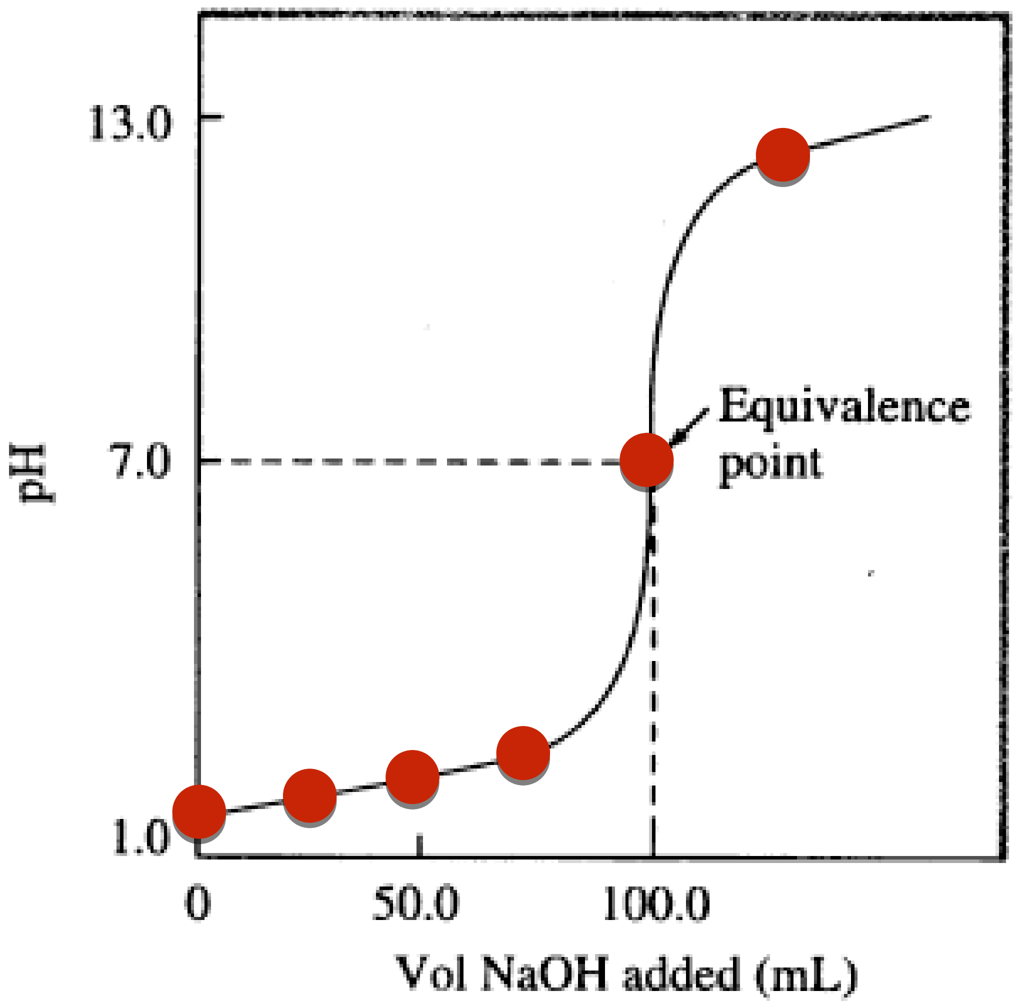
$[OH^-]$ = 0.0025 mol / 0.175 L = 0.014 M.

So, pOH = 1.85 and pH = 14 – 1.85 = 12.15.

Titration of strong acid with strong base

Summary so far:

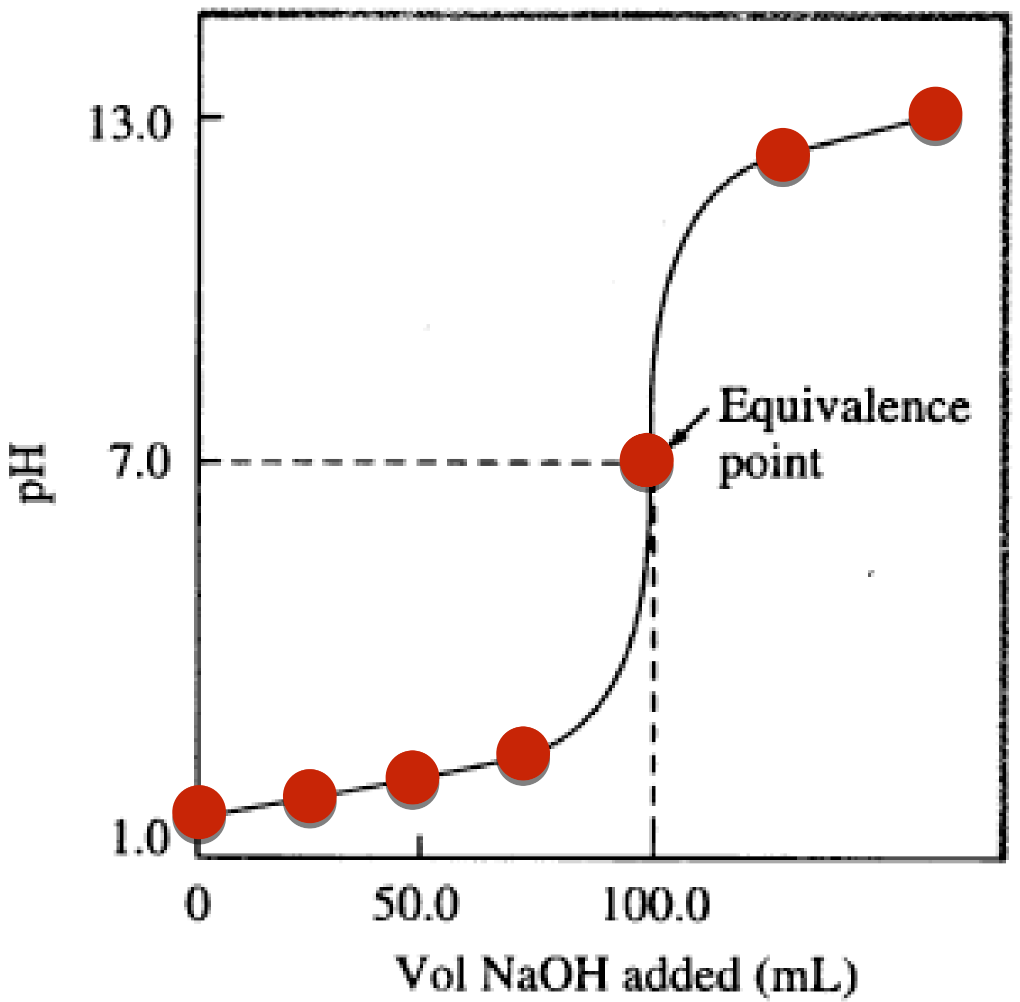
Vol NaOH added (mL)	pH	Vol NaOH added (mL)	pH
0.00	0.70	125.0	12.15
25.0	1.00		
50.0	1.30		
75.0	1.70		
100.0	7.00		



Titration of strong acid with strong base

We could keep calculating the volume & pH:

Vol NaOH added (mL)	pH	Vol NaOH added (mL)	pH
0.00	0.70	125.0	12.15
25.0	1.00	150.0	12.40
50.0	1.30	etc.	
75.0	1.70		
100.0	7.00		



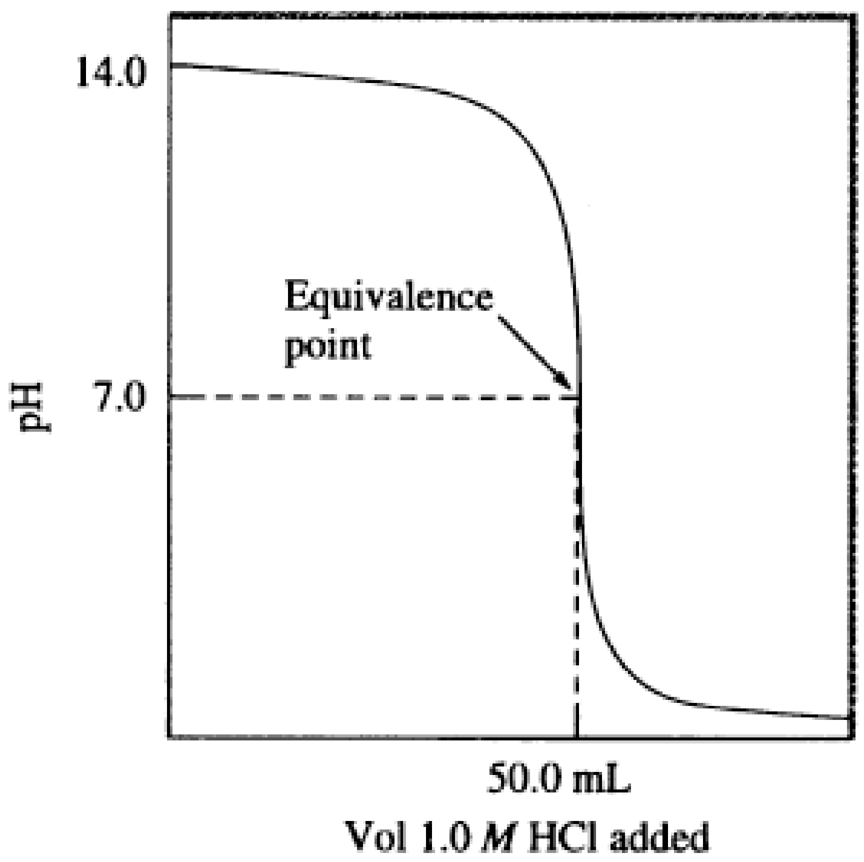
Titration of strong base with strong acid

Example. Titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl.

titrant (in buret)

Overview:

- Net reaction: $H_3O^+(aq) + OH^-(aq) \rightarrow 2H_2O(l)$
- Equivalence point again pH = 7
- Very large change in pH near equivalence point
- Before equivalence point the pH depends on excess of strong base
- After equivalence point the pH depends on excess of strong acid
- Titration curve calculation follows the same idea as we saw on previous slides



Titration of weak acid with strong base

Key to calculating weak acid/base titration curves:

- A strong base (or acid) reacts completely with a weak acid (or base)
- Then calculate as a new equilibrium (ICE table)

For titration of weak acid with strong base:

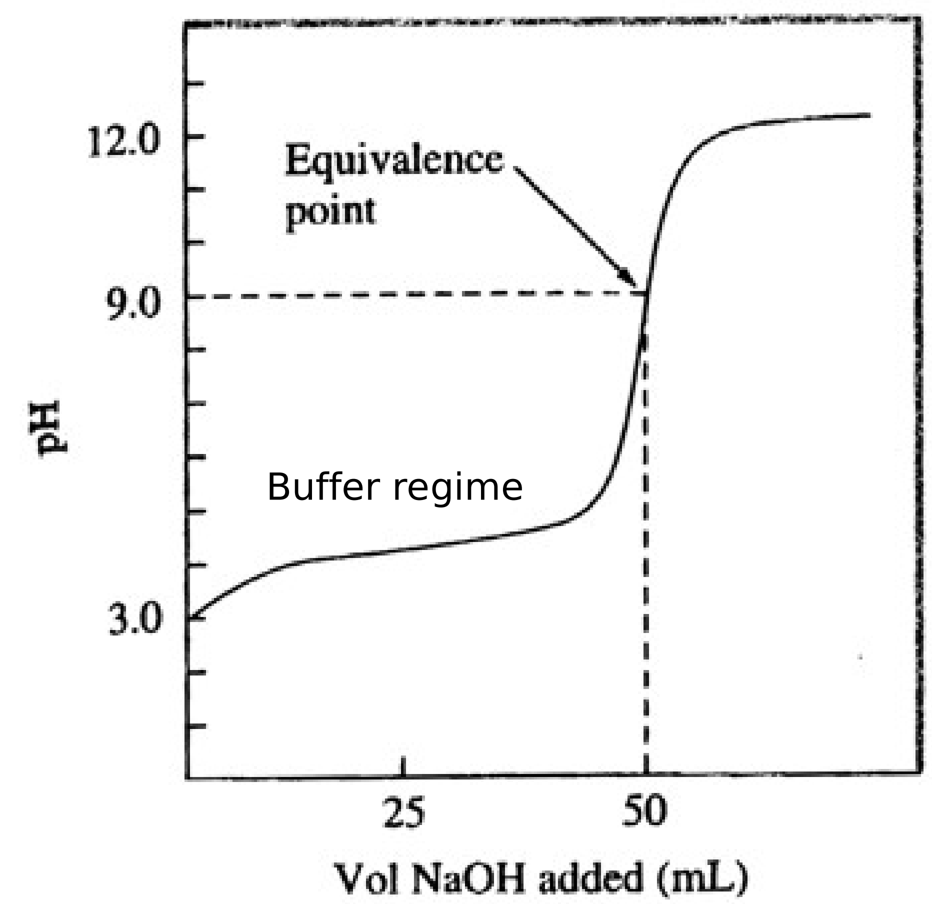
- pH at equivalence point will be > 7
- Weak acid / conjugate base buffer forms before the equivalence point

Titration of weak acid with strong base

Example. Titration of 50.0 mL of 0.100 M CH_3COOH with 0.100 M NaOH. titrant (in buret)

Overview:

- Net reaction: $CH_3COOH(aq) + OH^-(aq) \rightarrow 2H_2O(l) + CH_3COO^-(aq)$
- Equivalence point pH > 7
- Smaller change in pH near equivalence point
- Before equivalence point the pH is nearly constant (**buffer**)
- After equivalence point the pH depends on excess of strong base



Titration of weak acid with strong base

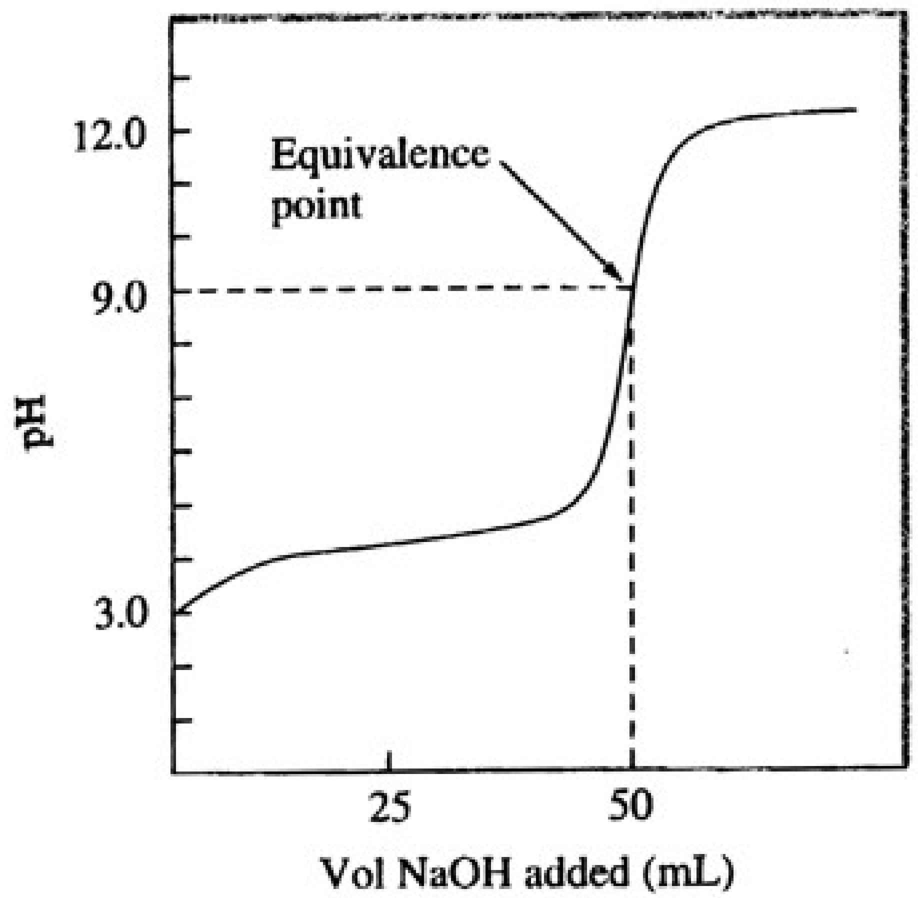
1. Equivalence point volume

$$moles\ acid = moles\ base$$

$$M_a V_a = M_b V_b$$

$$V_b = \frac{M_a V_a}{M_b} = \frac{(0.100\ M)(50.0\ mL)}{0.100\ M}$$

$$= 50.0\ mL$$

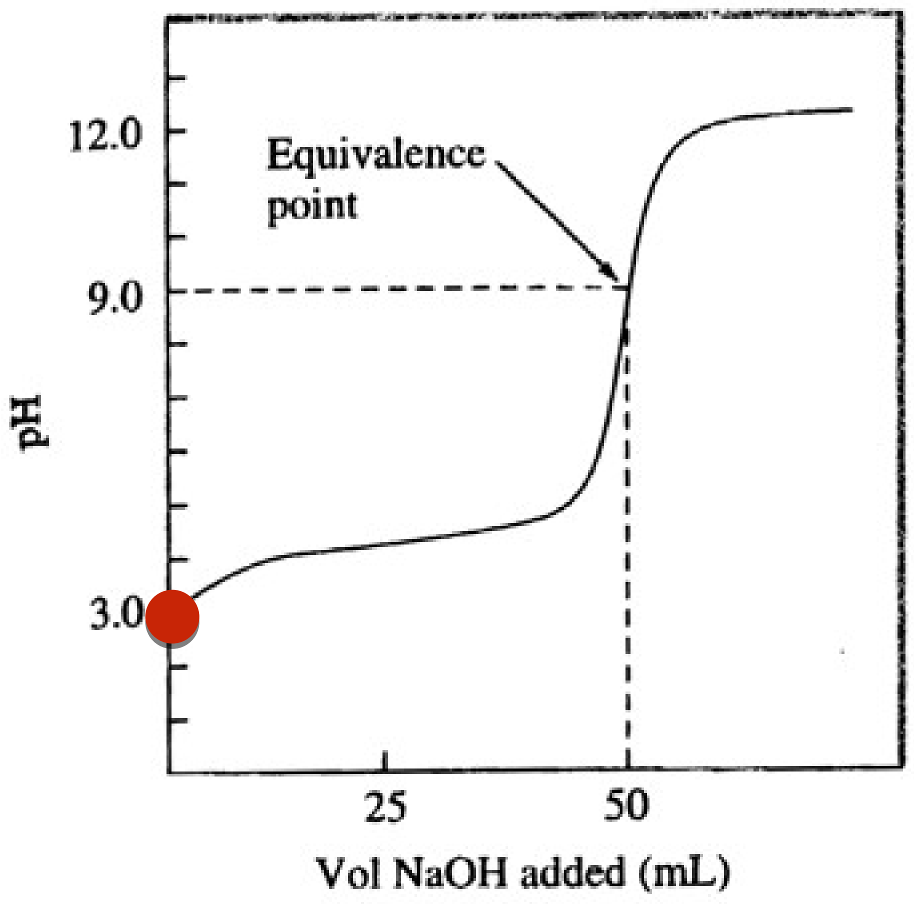


Titration of weak acid with strong base

2. Before adding any base

- $K_a = 1.8 \times 10^{-5}$ for CH_3COOH
- Treat as a weak acid equilibrium (ICE table problem)
- This would give pH = 2.87

(try solving this ICE table problem)



Titration of weak acid with strong base

3. Before equivalence point – add 15 mL of NaOH

Strong base converts some of the weak acid (HA) to its conjugate base (A^-).

Start with (0.0500 L HA)(0.100 mol/L) = 0.00500 mol of HA

Add 15 mL of NaOH (0.015 L)(0.100 M) = 0.0015 mol

(moles)	HA(*aq*)	+	OH^-(*aq*)	→	A^-(*aq*)
Before	0.005		--		--
Addition	--		0.0015		--
After	0.0035		0		0.0015

Titration of weak acid with strong base

We now have a solution with 0.0035 moles of HA and 0.0015 moles of A^- with new volume = 65.0 mL:

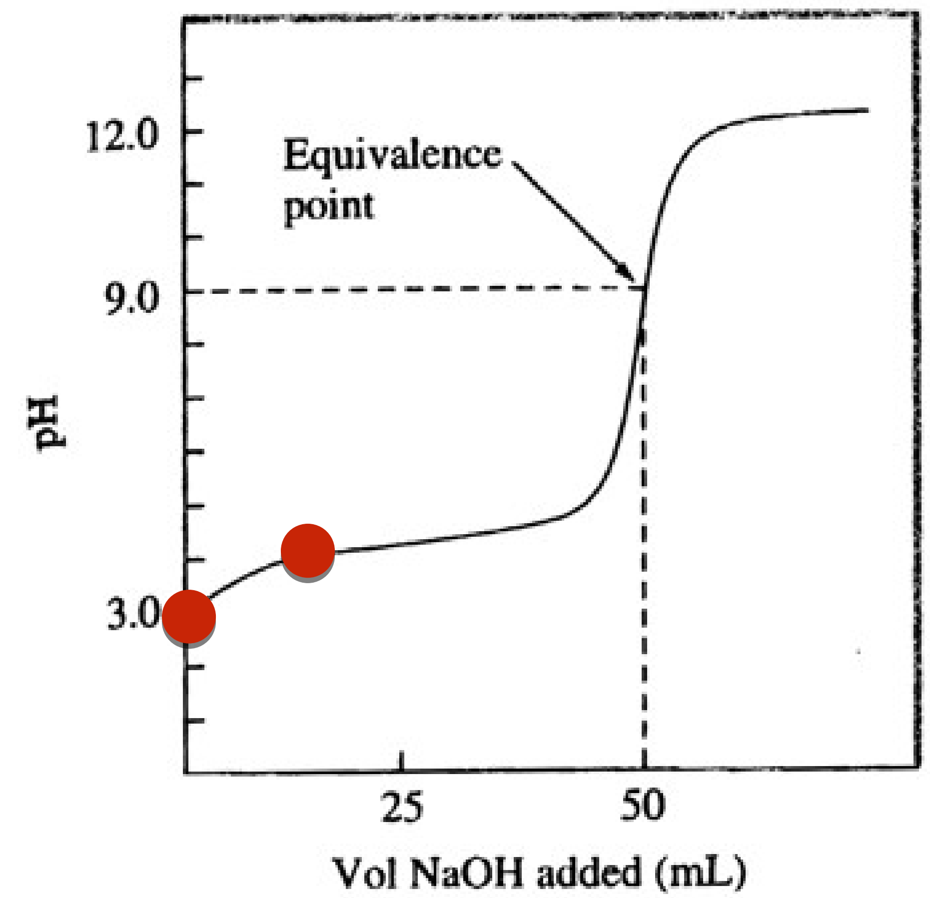
- *This is a buffer*! (when in doubt, use ICE table!!!)
- ICE chart or Henderson-Hasselbalch equation gives pH = 4.38.

Titration of weak acid with strong base

Summary so far:

pH = 2.87 at 0 mL of NaOH added

pH = 4.38 at 15 mL of NaOH added



Titration of weak acid with strong base

4. Before equivalence point – add 25 mL of NaOH

Strong base converts some of the weak acid to its conjugate base.

Start with (0.0500 L)(0.100 mol/L) = 0.00500 moles HA

Add 25 mL of NaOH (0.025 L)(0.100 M) = 0.0025 moles

We now have a solution with exactly equal HA and A^- (0.0025 mol of HA and 0.0025 mol of A^-).

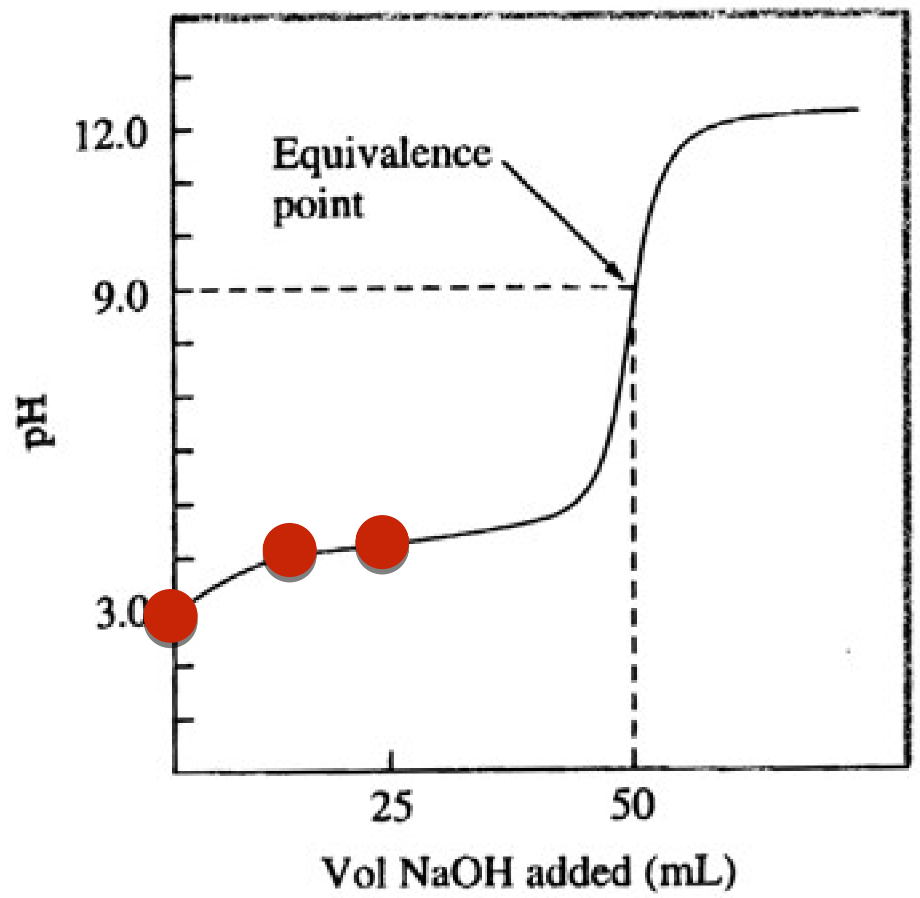
New volume = 75.0 mL.

ICE table calculation gives pH = 4.75.

Titration of weak acid with strong base

Summary so far:

Halfway to the equivalence point: pH = p*K*$_a$



Titration of weak acid with strong base

5. Before equivalence point – add 40 mL of NaOH

Strong base converts some of the weak acid to its conjugate base.

Start with (0.0500 L HA)(0.100 mol/L) = 0.00500 mol HA

Add 40 mL of NaOH (0.040 L)(0.100 M) = 0.0040 mol

We now have a solution with 0.0010 mol of HA and 0.0040 mol of A^-.

New volume = 50.0 mL + 40 mL = 90.0 mL.

ICE table gives pH = 5.34.

Titration of weak acid with strong base

6. At equivalence point – add 50 mL of NaOH

All of the weak acid has been converted to its conjugate base.

Start with (0.0500 L HA)(0.100 mol/L) = 0.00500 mol HA

Add 50 mL of NaOH (0.050 L)(0.100 M) = 0.00500 mol

We now have a solution with 0 moles of HA and 0.0050 moles of A^-.

New volume = 100.0 mL.

Set up an ICE table for the weak base, A^- (next slide).

Titration of weak acid with strong base

All of the weak acid has been converted to its conjugate base by the strong base:

$[A^-] = 0.0050 \text{ mol} / 0.100 \text{ L} = 0.050 \text{ M}.$

	$A^-(aq)$	$H_2O(l)$	$\rightleftharpoons$	$HA(aq)$	$OH^-(aq)$
I	0.050 M	-		0 M	0 M
C	$-x$	-		$+x$	$+x$
E	$0.050 - x$	-		x	x

$$K_b = \frac{K_w}{K_a} = 5.56 \times 10^{-10} = \frac{x^2}{0.050 - x}$$

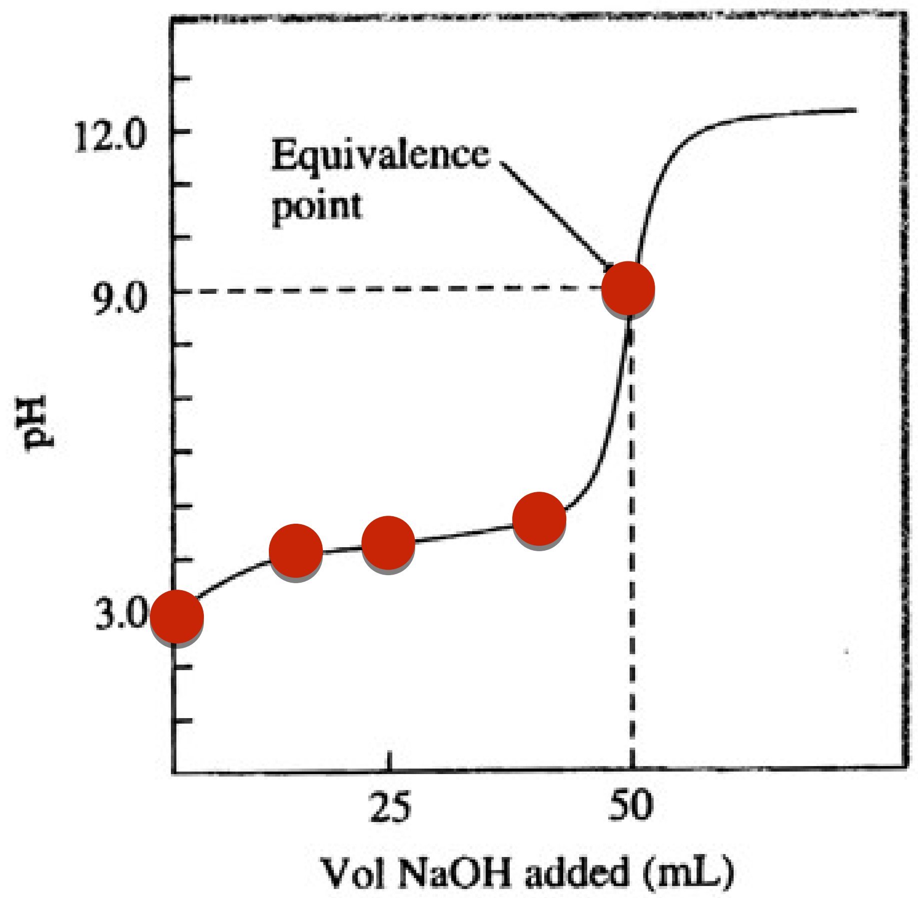
$$pH = 8.72$$

Solution is a weakly basic!

Titration of weak acid with strong base

Summary so far:

At the equivalence point: pH > 7 !



Titration of weak acid with strong base

7. Past equivalence point – add 75 mL of NaOH

Excess amount of *strong base*:

Start with (0.0500 L HA)(0.100 mol/L) = 0.00500 mol HA

Add 75 mL of NaOH (0.075 L)(0.100 M) = 0.00750 mol

We now have a solution with:

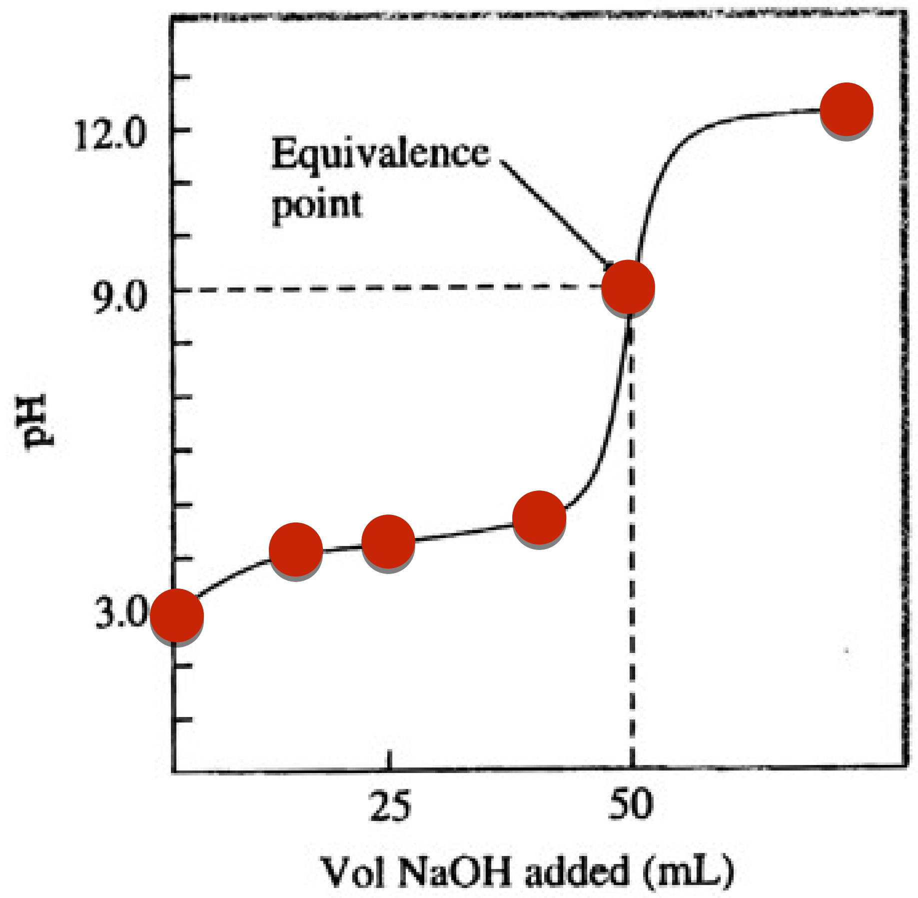
- 0 moles of HA and 0.00750 – 0.00500 = 0.00250 excess moles of OH^-.
- New volume = 125.0 mL.
- $[OH^-]$ = 0.020 M, pOH = 1.70, pH = 14 – 1.70 = 12.3.

Excess of strong base

Titration of weak acid with strong base

Summary:

The pH at the equivalence point is not 7 but 9!



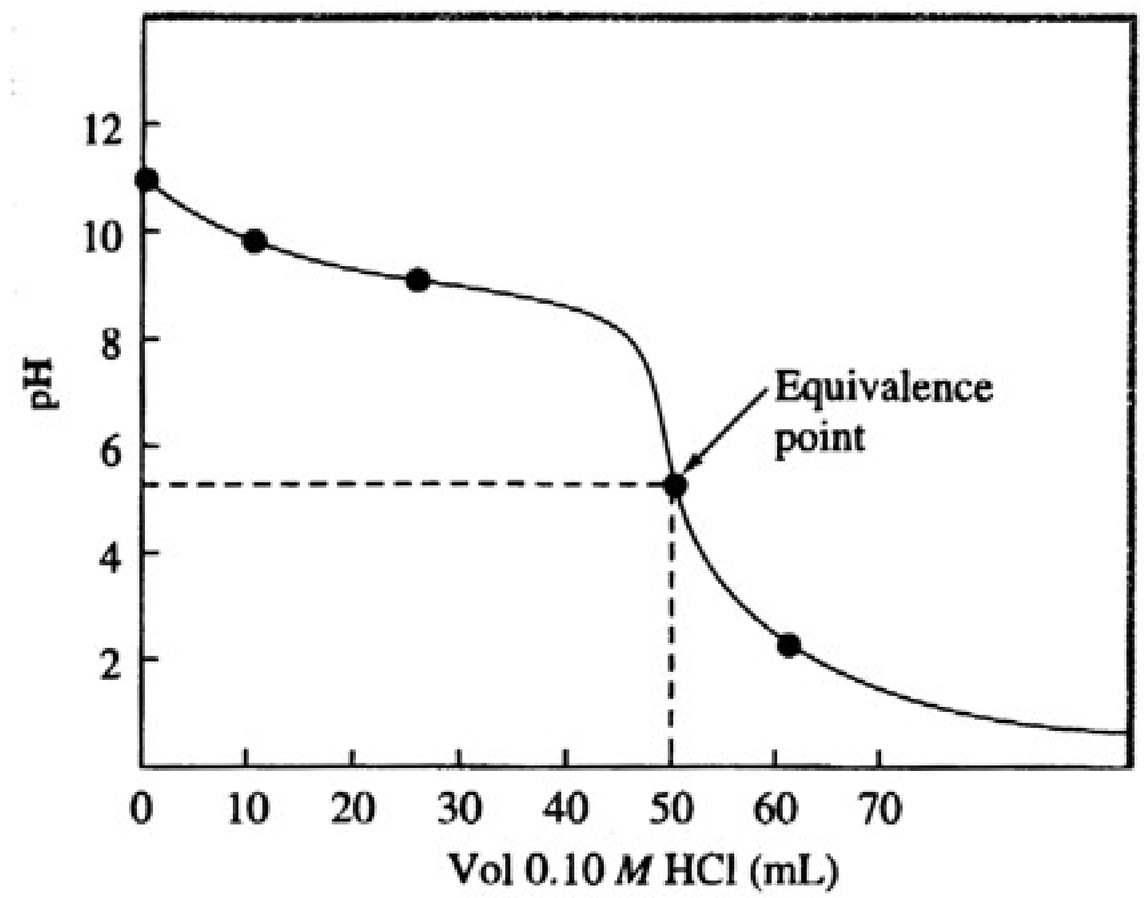
Titration of weak base with strong acid

Example: Titration of 100.0 mL of 0.05 M NH_3 with 0.10 M HCl. ← titrant (in buret)

Overview:

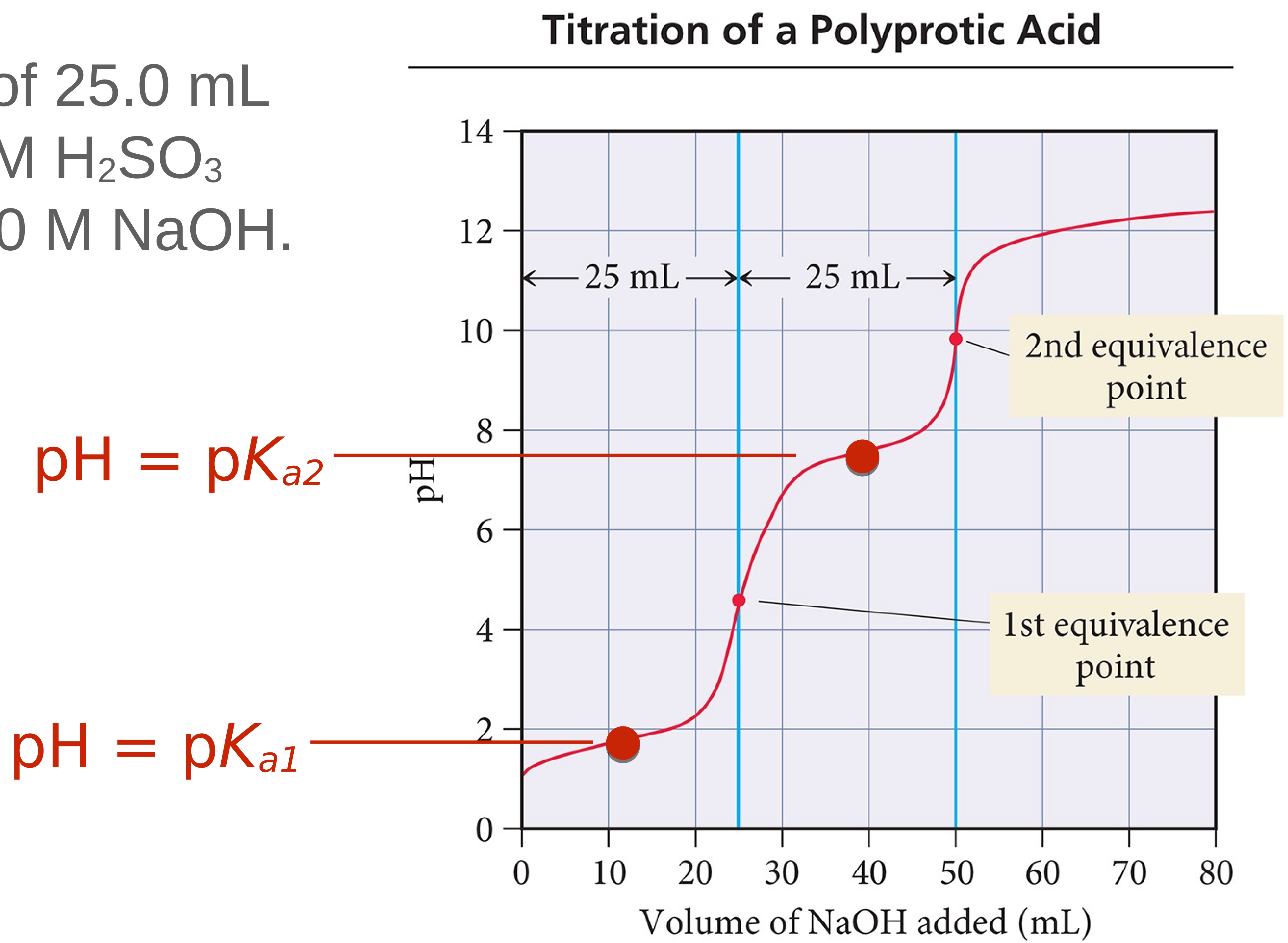
- Net reaction: $NH_3(aq) + H_3O^+(aq) \rightarrow H_2O(l) + NH_4^+(aq)$
- Equivalence point pH < 7
- At equivalence point: All weak base has been converted to weak acid.
- Halfway to equivalence point: $[BH^+] = [B]$, pH = pK_a of acid.

$$pH = pK_a + log\left(\frac{[B]}{[BH^+]}\right)$$ (buffer)



Titration of polyprotic acids

Titration of 25.0 mL of 0.100 M H_2SO_3 with 0.100 M NaOH.



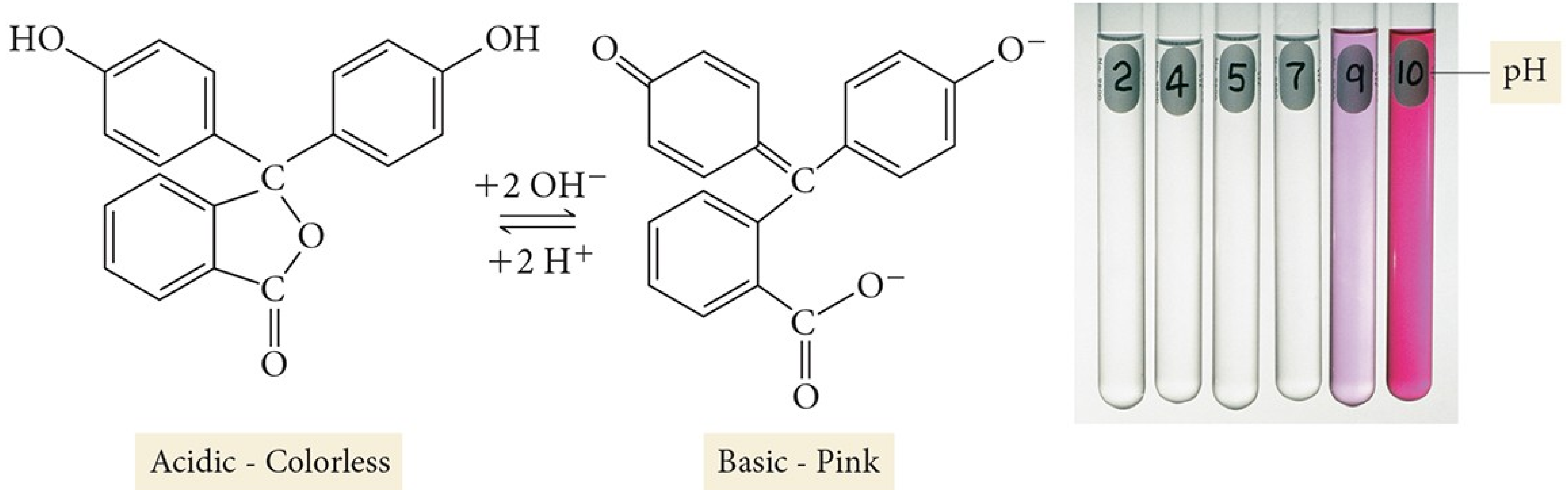
Indicators

- Color of some compounds depends on the pH
- Can use this to determine the equivalence point of a titration:

$$HIn(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + In^-(aq)$$

Color 1 Color 2

Phenolphthalein, a Common Indicator



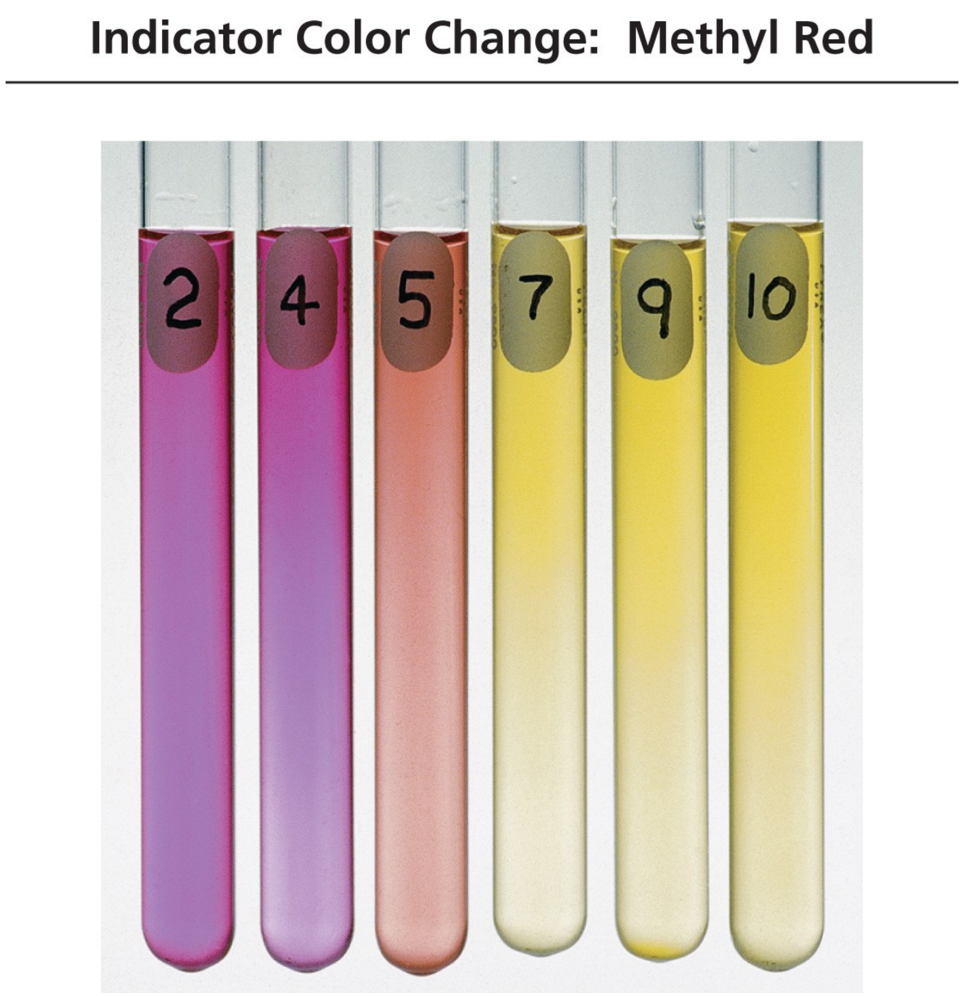
Indicators

What is the pH range over which methyl red indicator ($K_a = 7.9 \times 10^{-6}$) changes from pink (acid form) to yellow (basic form)?

$pK_a = -\log(7.9 \times 10^{-6}) = 5.1$

Color changes at $pK_a \pm 1$

It will be pink at pH = 4.1 (and below) and yellow at pH 6.1 (and above)



pH = pK_a when $[In^-] = [HIn]$

Using an Indicator

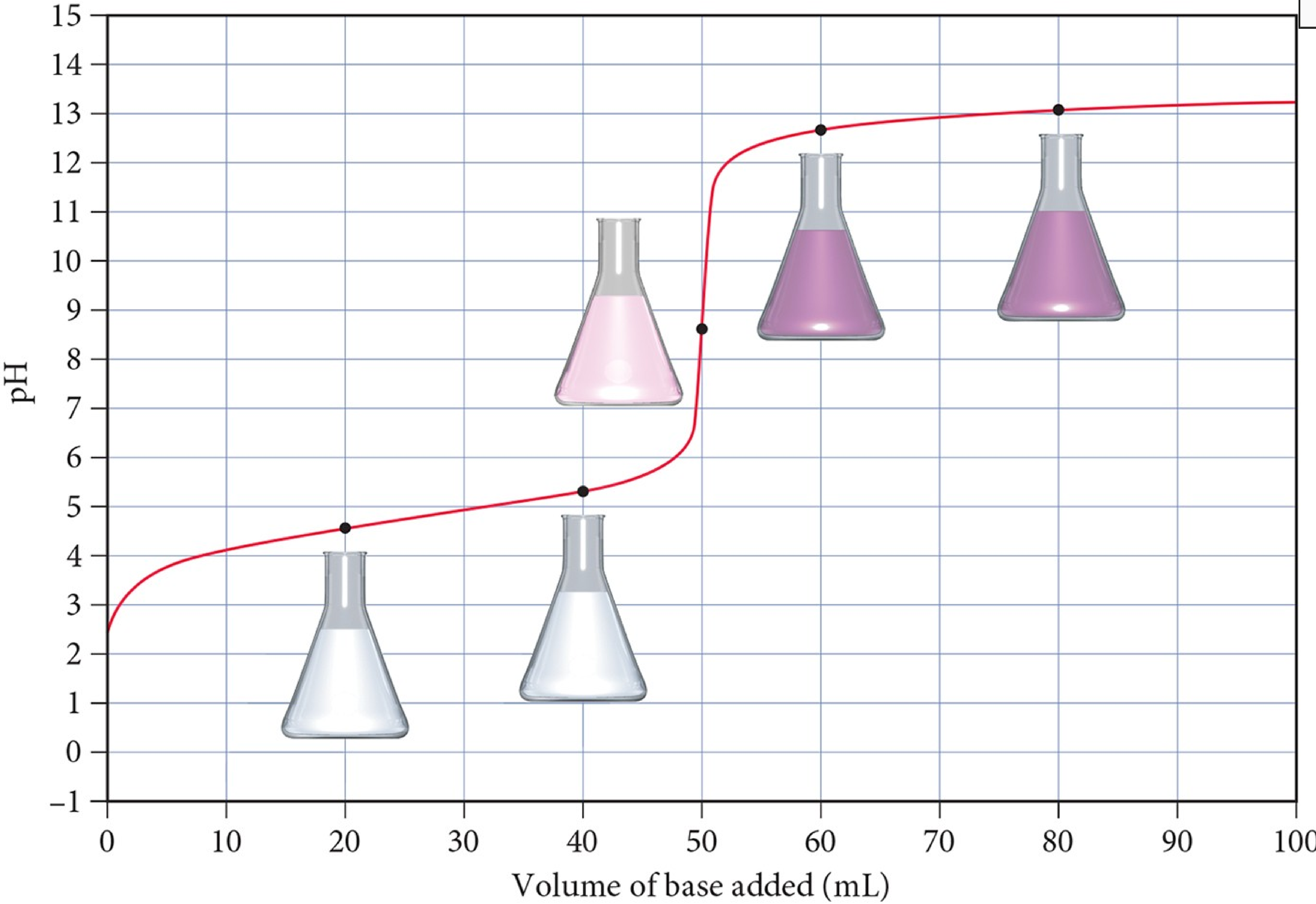
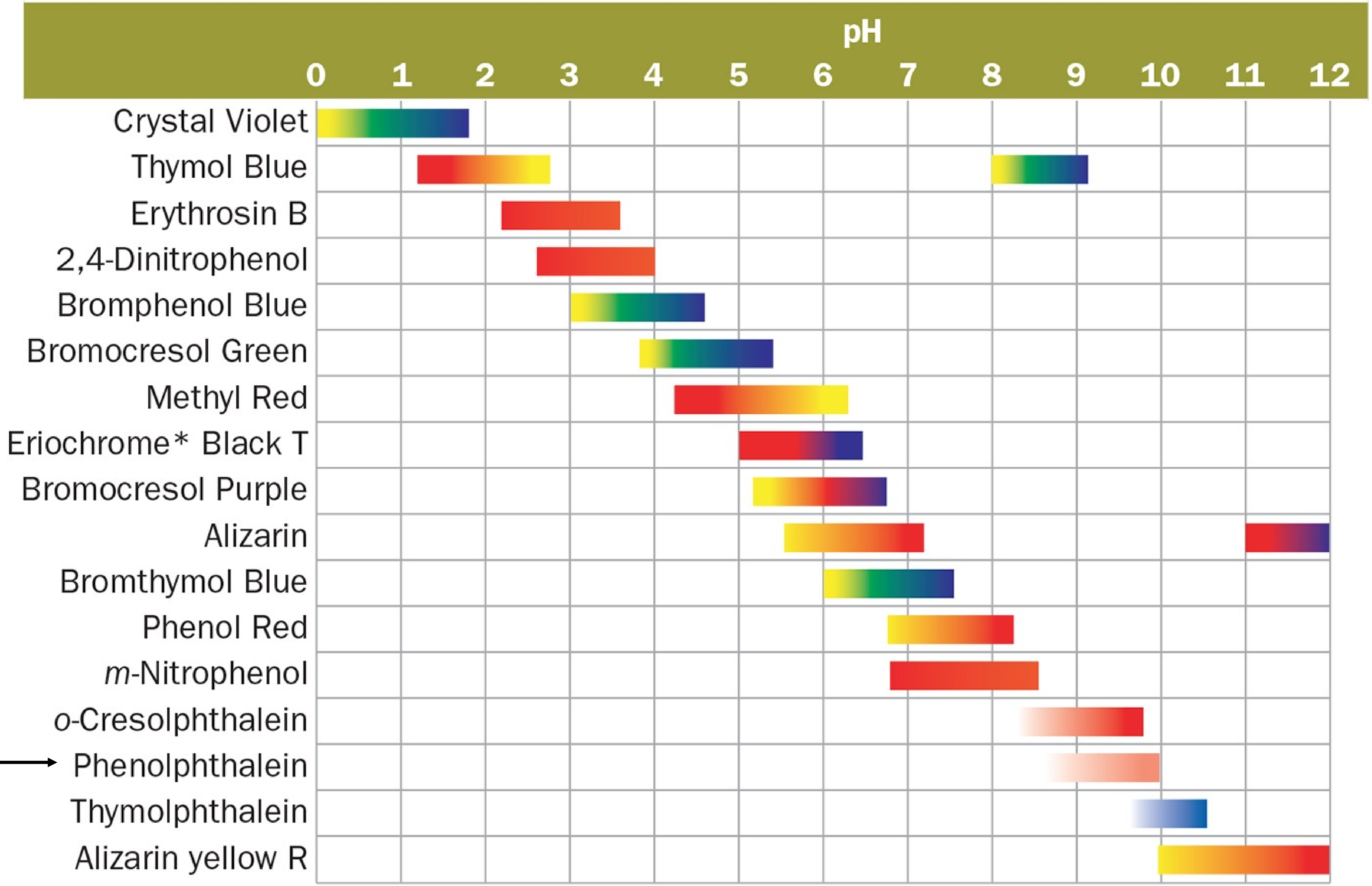


TABLE 17.1 Ranges of Color Changes for Several Acid–Base Indicators



*Trademark of CIBA GEIGY CORP.

pH (relative to pK_a)	$[In^-]/[HIn]$ ratio	Color of Indicator Solution
$pH = pK_a$	$\frac{[In^-]}{[HIn]} = 10^0 = 1$	Intermediate color
$pH = pK_a + 1$ (and above)	$\frac{[In^-]}{[HIn]} = 10^1 = 10$	Color of In^-
$pH = pK_a - 1$ (and below)	$\frac{[In^-]}{[HIn]} = 10^{-1} = 0.10$	Color of HIn

Note: If we have a pH meter, we can use that instead of indicator.