Topic 6G. Buffers

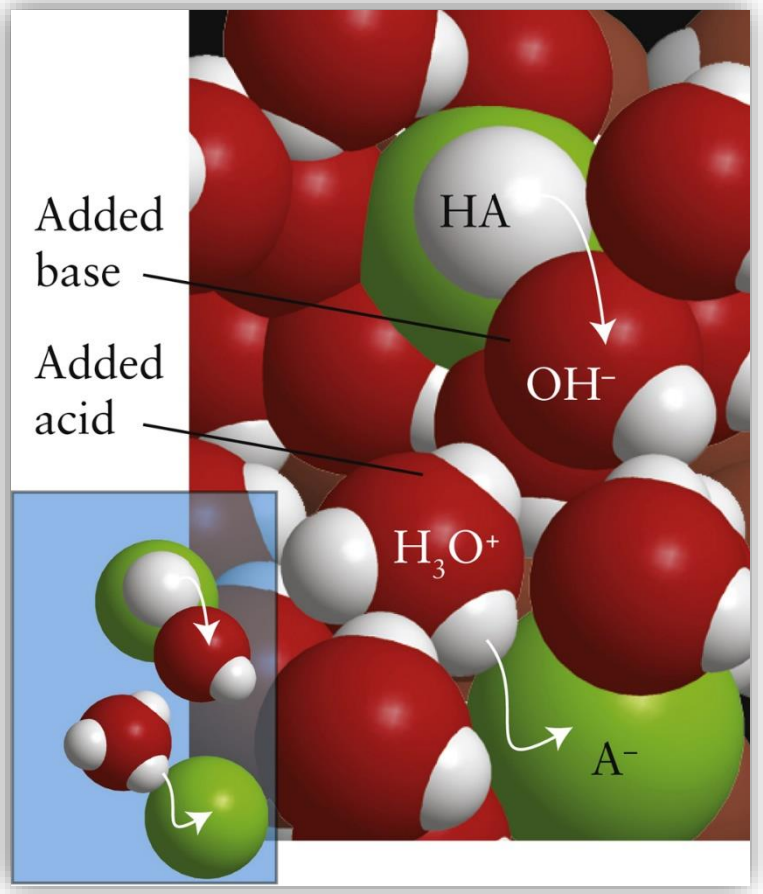
6G.1 Buffer Action

6G.2 Designing a Buffer

6G.3 Buffer Capacity

Buffer Action

- Buffer: a mixed solution in which the pH resists change when small amounts of strong acids or bases are added.
  - Consists of an aqueous solution of a weak acid and its conjugate base supplied as a salt, or a weak base and its conjugate acid supplied as a salt.
  - Functions as a sink for or source of protons
  - Could an aqueous solution of glycine, $^{-}O_2CCH_2NH_3^{+}$, which contains both acidic and basic groups, act as a buffer?



Designing a Buffer

- Acid buffer consists of a weak acid and its conjugate base provided as a salt.
  Ex) 0.05 M CH_3COOH (aq) + 0.05 M CH_3COONa (aq)
- Base buffer consists of a weak base and its conjugate acid provided as a salt.
  Ex) 0.05 M NH_3 (aq) + 0.05 M NH_4Cl (aq)

Designing a Buffer

- Equimolecular buffer solution with the same concentrations of the conjugate acid and base.

$$HA\ (aq) + H_2O\ (l) \leftrightarrow H_3O^+\ (aq) + A^-\ (aq)$$

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a \approx \frac{[H_3O^+][A^-]_{initial}}{[HA]_{initial}} \overset{\text{Cancel blue terms}}{=} [H_3O^+]$$

$$pH = pK_a$$

Designing a Buffer

TABLE 6G.1 The Composition of Buffers

	Composition	Calculate pH from…	Examples	pK_a
Acid buffers (for pH < 7)				
acid (HA)	conjugate base (A^-) as the salt MA	pK_a(HA)	$CH_3COOH/CH_3CO_2^-$	4.75
			HNO_2/NO_2^-	3.37
			$HClO_2/ClO_2^-$	2.00
Base buffers (for pH > 7)				
base (B)	conjugate acid (HB^+) as the salt HBX	$pK_a(HB^+)$ by using $pK_a(HB^+) + pK_b(B) = pK_w$	NH_4^+/NH_3	9.25
			$(CH_3)_3NH^+/(CH_3)_3N$	9.81
			$H_2PO_4^-/HPO_4^{2-}$	7.21

Designing a Buffer

- Henderson–Hasselbalch equation

$$HA\ (aq) + H_2O\ (l) \leftrightarrow H_3O^+\ (aq) + A^-\ (aq)$$

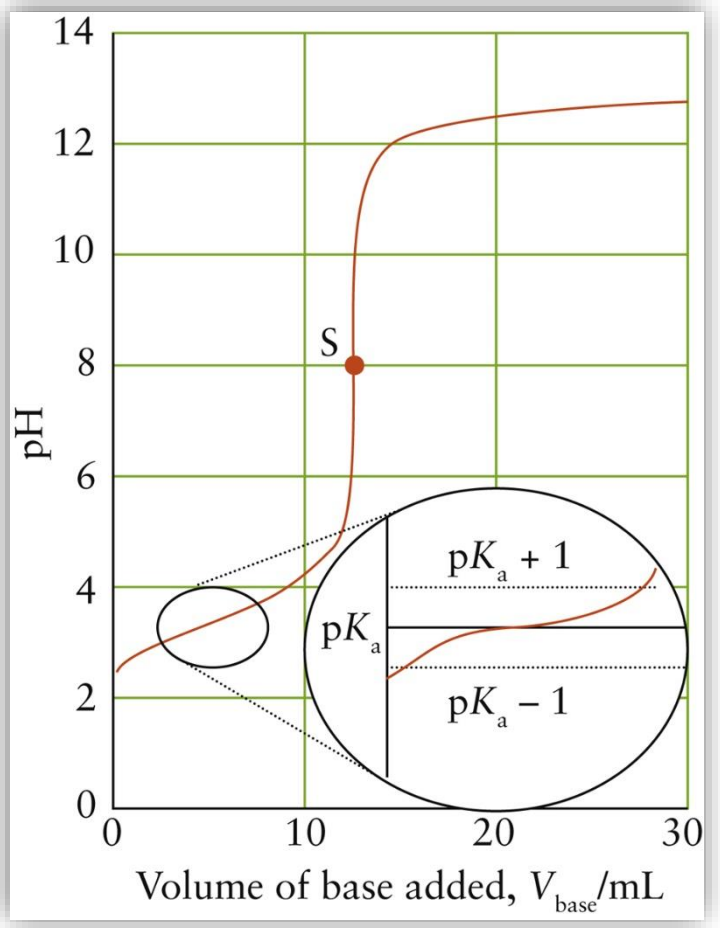
$$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

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

$$pH \approx pK_a + \log\frac{[base]_{initial}}{[acid]_{initial}}$$

Buffer Capacity

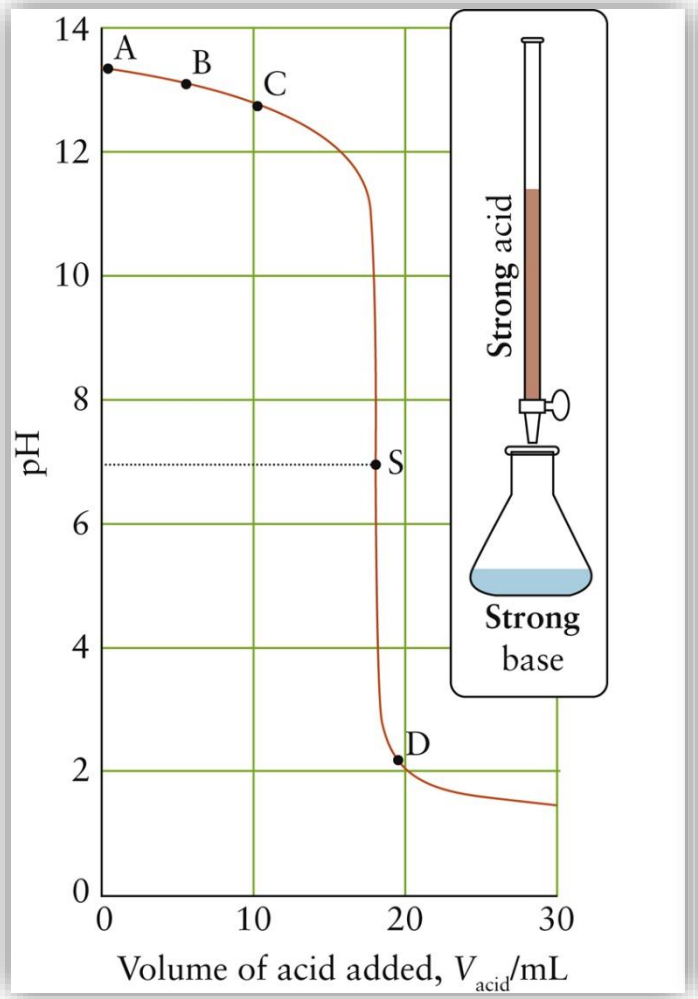
- Buffer capacity: the maximum amount of acid or base that can be added before the buffer loses its ability to resist large changes in pH

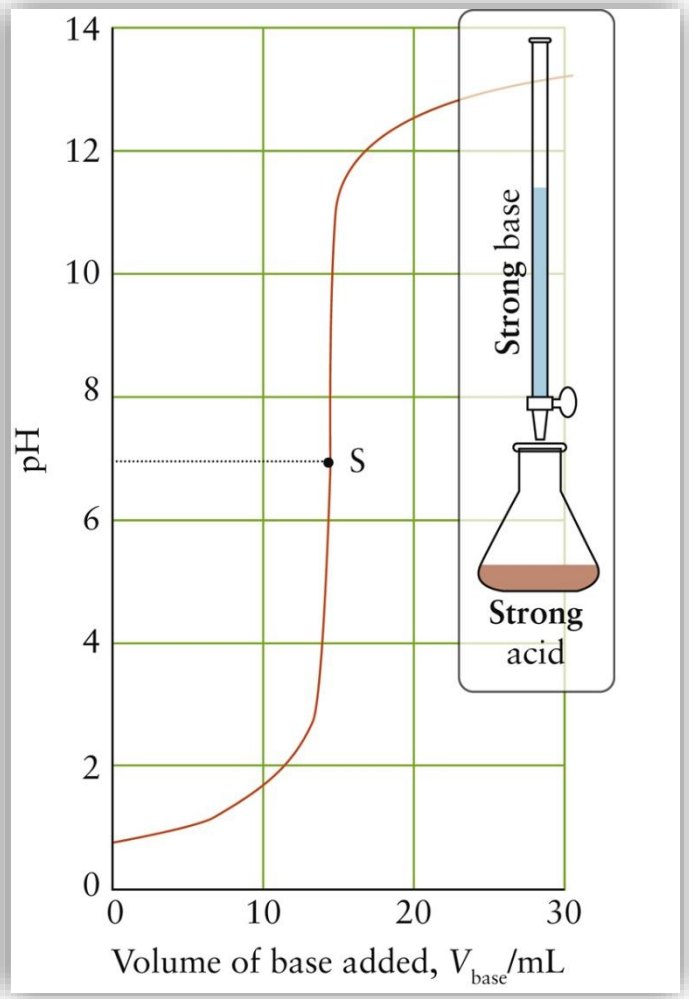


Topic 6H. Acid–Base Titration

Strong Acid–Strong Base Titrations

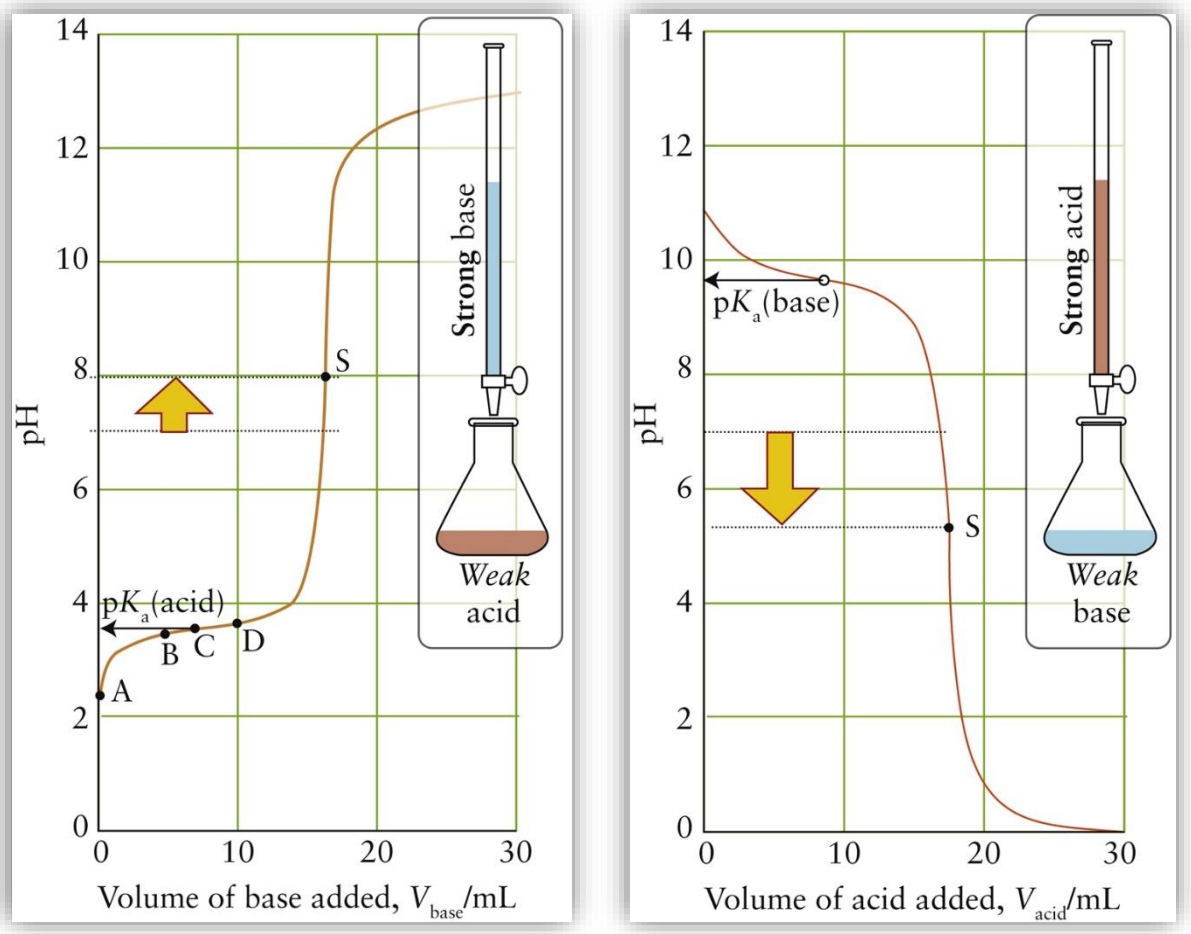
- pH curve: a plot of the pH of the analyte solution against the volume of titrant added during a titration.
- In strong acid-base titration, the pH changes slowly initially, changes rapidly through pH = 7 at the stoichiometric point, and then changes slowly again.



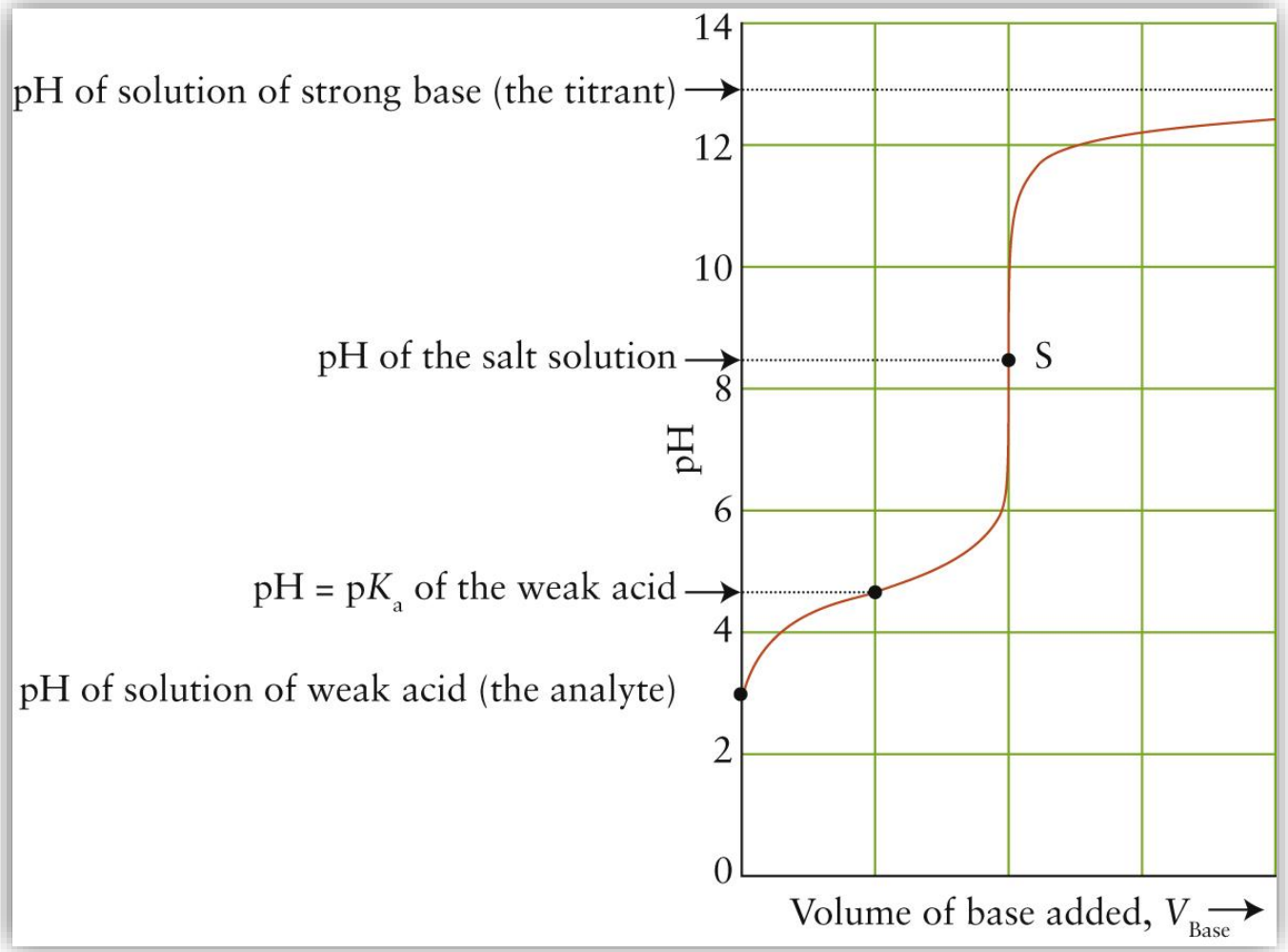


Strong Acid–Weak Base and Weak Acid–Strong Base

- Titration of a weak acid with strong base: the pH is greater than 7 at the stoichiometric point.
- Titration of a weak base with strong acid: the pH is less than 7 at the stoichiometric point.



Strong Acid–Weak Base and Weak Acid–Strong Base



Strong Acid–Weak Base and Weak Acid–Strong Base

TABLE 6H.1 Weak Acid and Weak Base Titration Equilibria

Point in titration	Primary species	Proton transfer equilibrium	Related Toolbox
1 Weak acid HA titrated with strong base			
initial	HA	$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$	6D.1
buffer region	HA, A^-	$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$	6H.2
stoichiometric point	A^-	$A^-(aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq)$	6D.2
At the stoichiometric point, the solution is of a salt with a basic anion			
2 Weak base B titrated with strong acid			
initial	B	$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$	6D.2
buffer region	B, HB^+	$B(aq) + H_2O(l) \rightleftharpoons HB^+(aq) + OH^-(aq)$	6H.2
stoichiometric point	HB^+	$HB^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + B(aq)$	6D.1
At the stoichiometric point, the solution is of a salt with an acidic anion			

Acid–Base Indicators

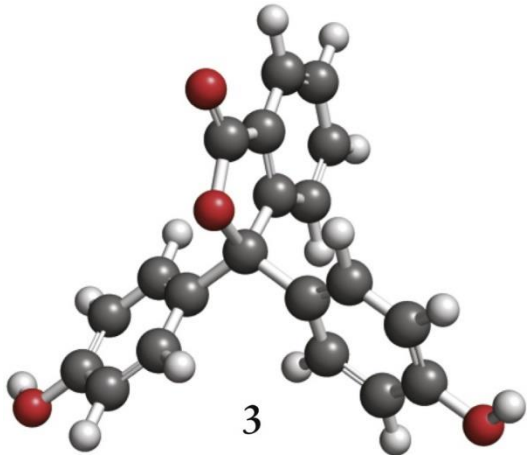
- Acid–base indicator
  - A water- soluble dye with a color that depends on the pH.
  - A weak acid that has one color in its acid form (HIn) and another color in its conjugate base form (In^-)

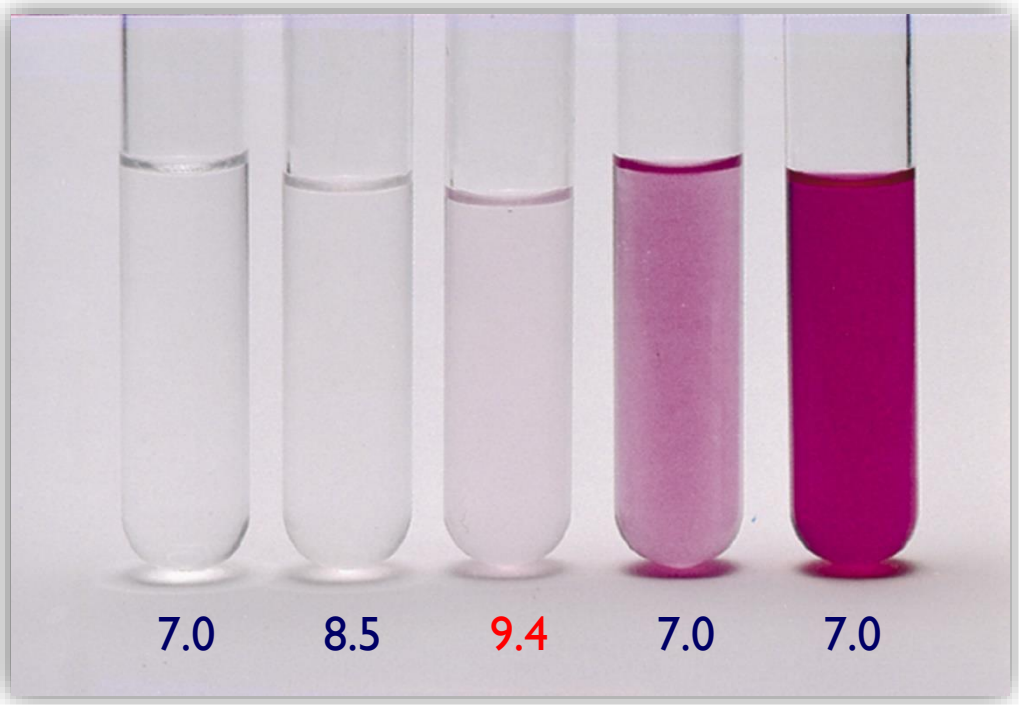
    $HIn\ (aq) + H_2O\ (l) \leftrightarrow H_3O^+\ (aq) + In^-\ (aq)$

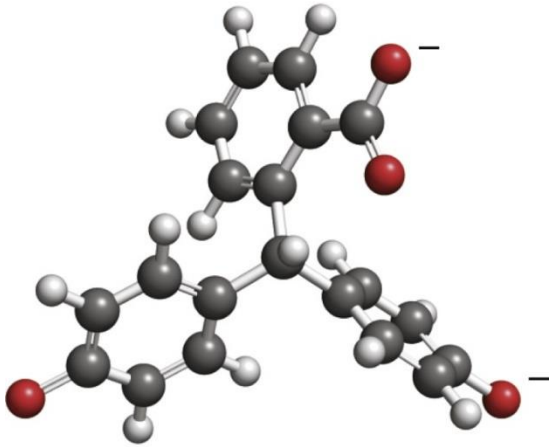
    At end point, $[HIn] = [In^-] \rightarrow [H_3O^+] = pH = pK_{In}$

Acid–Base Indicators

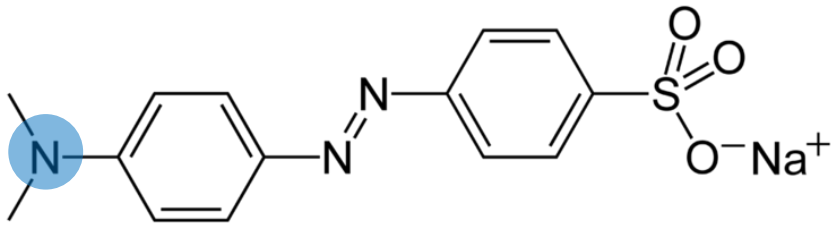
- Phenolphthalein



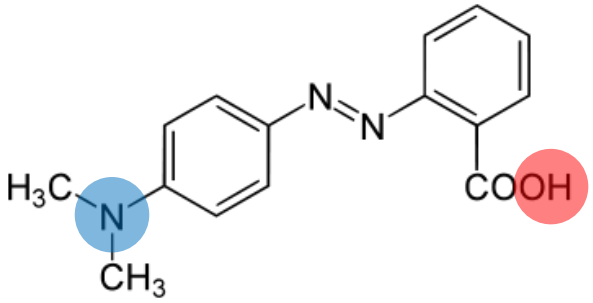




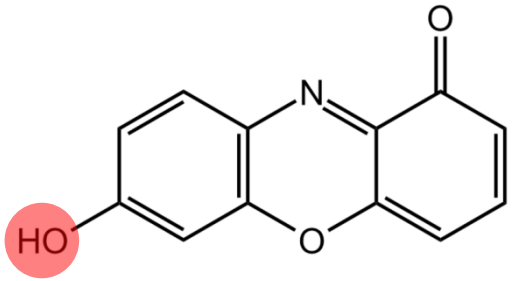
Acid–Base Indicators



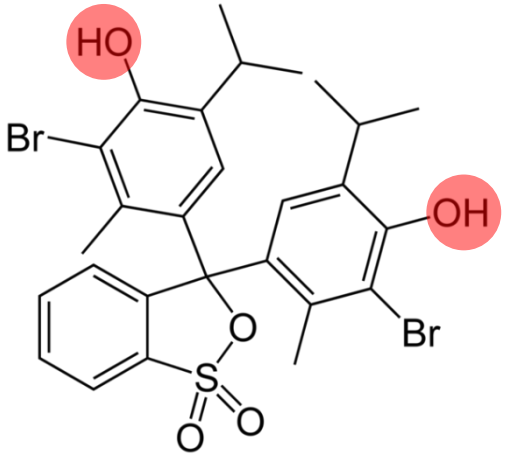
Methyl orange



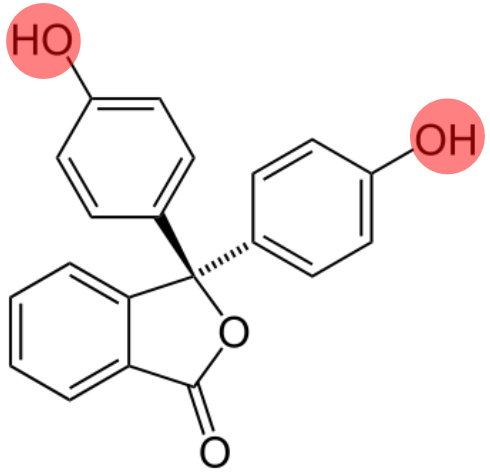
Methyl red



Litmus



Bromothymol blue



Phenolphthalein

Acid–Base Indicators

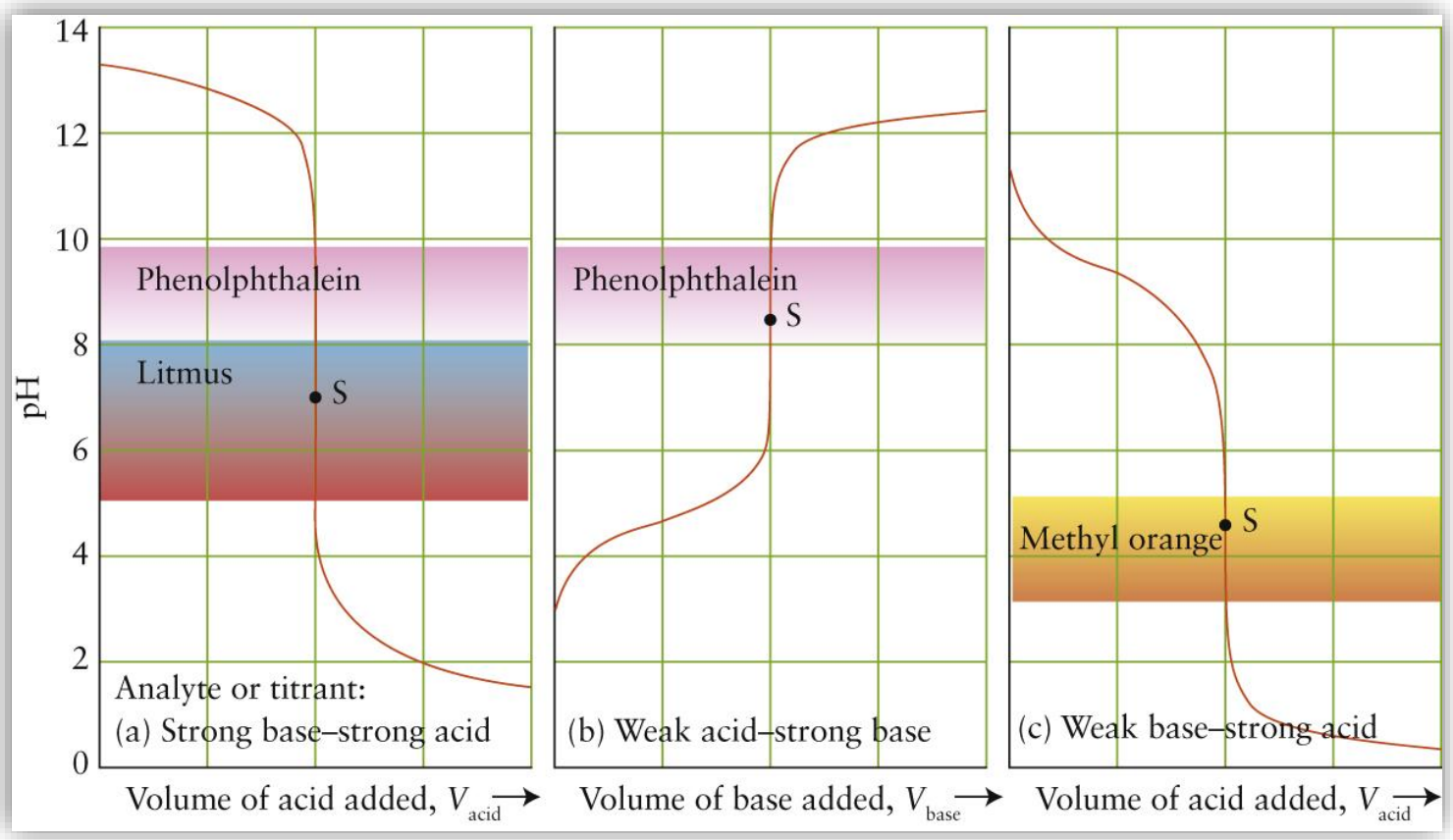
TABLE 6H.2 Indicator Color Changes*

Indicator	pK_{In}	pH range of color change	Color of acid form		Color of base form
thymol blue	1.7	1.2 to 2.8	red		yellow
methyl orange	3.4	3.2 to 4.4	red		yellow
bromophenol blue	3.9	3.0 to 4.6	yellow		blue
bromocresol green	4.7	3.8 to 5.4	yellow		blue
methyl red	5.0	4.8 to 6.0	red		yellow
litmus	6.5	5.0 to 8.0	red		blue
bromothymol blue	7.1	6.0 to 7.6	yellow		blue
phenol red	7.9	6.6 to 8.0	yellow		red
thymol blue	8.9	8.0 to 9.6	yellow		blue
phenolphthalein	9.4	8.2 to 10.0	colorless		pink
alizarin yellow R	11.2	10.1 to 12.0	yellow		red
alizarin	11.7	11.0 to 12.4	red		purple

Acid–Base Indicators

- Recommended indicator

  pK_{In} = pH (at the stoichiometric point) ± 1



Polyprotic Acid Titrations

- Titration of a solution of the dichloride salt of the amino acid histidine, $C_6H_{11}N_3O_2Cl_2$ (aq) [H_3A^{2+}], with a solution of NaOH.

H_3A^{2+} (aq) + OH^- (aq) → H_2A^+ (aq) + H_2O (l)

H_2A^+ (aq) + OH^- (aq) → HA (aq) + H_2O (l)

HA (aq) + OH^- (aq) → A^- (aq) + H_2O (l)