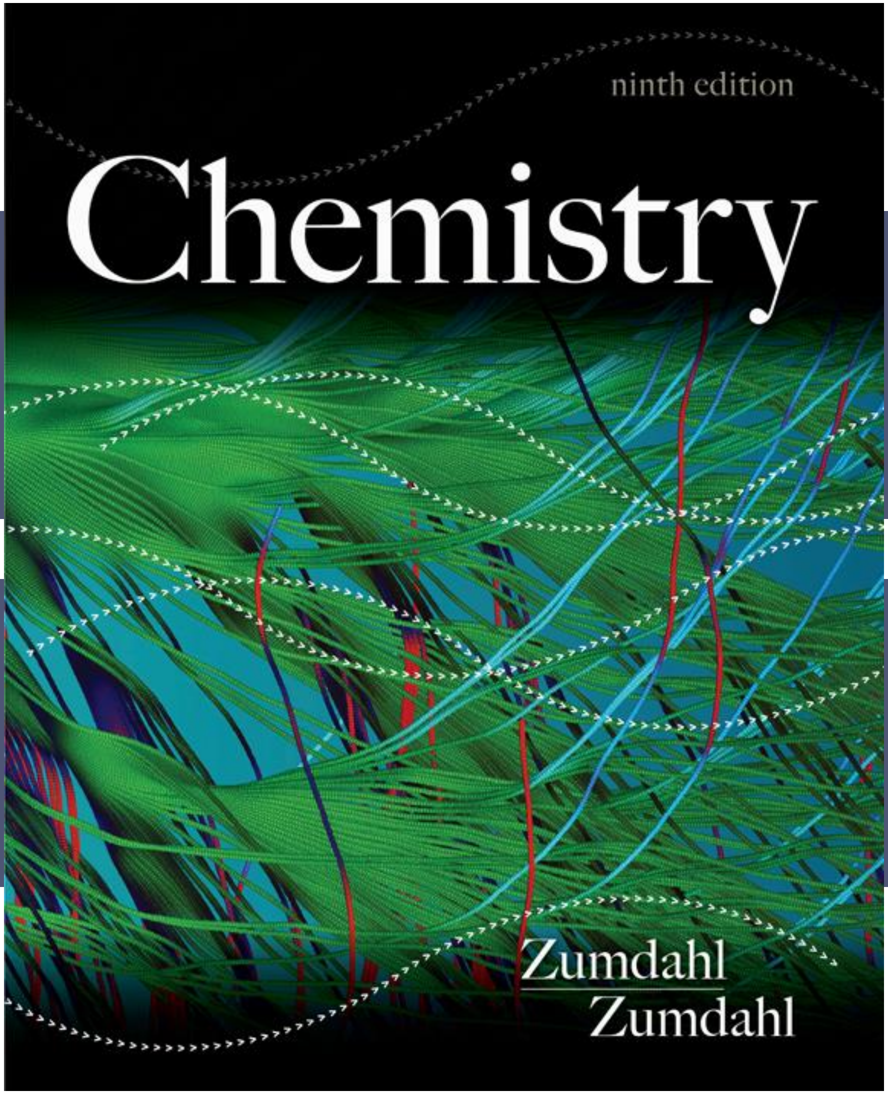


Chapter 15

Acid-Base Equilibria

Common Ion Effect

- Shift in equilibrium position that occurs because of the addition of an ion already involved in the equilibrium reaction.
- An application of Le Châtelier’s principle.

Example:

$$HCN_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + CN^-_{(aq)}$$

- Addition of NaCN will shift the equilibrium to the left because of the addition of CN^-, which is already involved in the equilibrium reaction.
- A solution of HCN and NaCN is less acidic than a solution of HCN alone.

Key Points about Buffered Solutions

- Buffer solutions resist a change in pH.
- They are weak acids or wek bases containing a common ion.
- *OR* Buffers are mixtures of:

A weak acid and its conjugate base

OR A weak base and its conjugate acid

- For a good buffer, both components should be of high concentrations.

Henderson–Hasselbalch Equation:

Consider the general weak acid equilibrium below:

$$\mathrm{HA}_{(aq)} \rightleftharpoons \mathrm{H}^{+}_{(aq)} + \mathrm{A}^{-}_{(aq)}$$

$$Ka = \frac{[H^{+}][A^{-}]}{[HA]}$$

$$[H^{+}] = Ka\frac{[HA]}{[A^{-}]}$$

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

- For a particular buffering system (conjugate acid–base pair), all solutions that have the same ratio $[A^{-}] / [HA]$ will have the same pH.

- For the general weak base/conjugate acid buffer, B/HB^+:

$$B_{(aq)} + H_2O_{(aq)} \rightleftharpoons HB^+_{(aq)} + OH^-_{(aq)}$$

$$K_b = \frac{[HB][OH^-]}{[B]}$$

$$[OH^-] = K_b \frac{[B]}{[HB^+]}$$

$$pOH = pK_b + \log \frac{[HB^+]}{[B]}$$

For a particular weak base/conjugate acid buffer, the pOH is a function of the ratio of the concentrations of HB^+/B.

What is the pH of a buffer solution that is 0.45 *M* acetic acid ($HC_2H_3O_2$) and 0.85 M sodium acetate ($NaC_2H_3O_2$)? The K_a for acetic acid is 1.8×10^{-5}.

$CH_3COONa_{(aq)} \rightarrow CH_3COO^-{}_{(aq)} + Na^+{}_{(aq)}$

0.85 M

$CH_3COOH_{(aq)} \rightleftharpoons H^+{}_{(aq)} + CH_3COO^-{}_{(aq)}$

0.45 - x x x

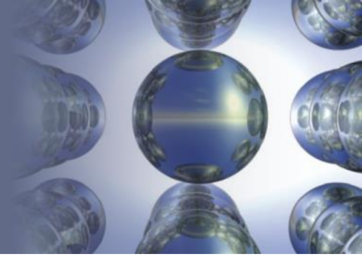
$K_a = [H^+][CH_3COO^-]/[CH_3COOH]$

$[H^+] = x$; $[CH_3COO^-] = (x + 0.85\ M) \approx 0.85\ M$

$[H^+] = K_a([CH_3COOH]/[CH_3COO^-]$

$= (1.8x10^{-5})(0.45/0.85) = 9.53x10^{-6}$

pH = - log ($9.53x10^{-6}$) = 5.02 acidic



Addition of strong acid to a buffer solution:

A) Calculate the pH of a buffer solution that is 0.50 M acetic acid and 0.55 M sodium acetate? $K_a = 1.75\text{x}10^{-5}$.

B) Calculate the change in pH of the buffer in (A) when 0.480 g NaOH is added to 1 L of the buffer?

C) Calculate the change in pH of the buffer in (A) when 0.480 g NaOH is added to 1 L of H_2O? Comment on the results.

Solution:

A) $pH = pK_a + \log\frac{[A^-]}{[HA]} = -\log(1.75\text{x}10^{-5}) + \log 0.55/0.50$

$= +4.76 + 0.041 = 4.80$

B) Upon addition of 0.48g NaOH to 1 L of the buffer:

0.48 g = 0.012 mol. NaOH, the volume of the solution is 1.0 L.

NaOH will react with the acidic part of the buffer with 1:1 ratio, so the $[CH_3COOH]$ will decrease by 0.012 M and $[CH_3COO^-]$ will increase by 0.012 M.

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

$[CH_3COOH] = 0.50 – 0.012 = 0.488$ M

$[CH_3COO^-] = 0.55 + 0.012 = 0.562$ M

$$[H^+] = K_a \frac{[HA]}{[A]} = (1.75x10^{-5}) \frac{0.488}{0.562} = 1.52x10^{-5}$$

pH = $-\log(1.52x10^{-5}) = 4.82$

Δ pH = 4.80 − 4.82 = 0.020

C) Upon addition of 0.48g NaOH to 1 L of water:

0.48 g = 0.012 mol. NaOH, the volume of the solution is 1.0 L.

$[OH^-] = 0.012$ M, so,

$[H^+] = 1x10^{-14}/0.012 = 8.33x10^{-13}$

$pH = - \log (8.33x10^{-13}) = 12.08$

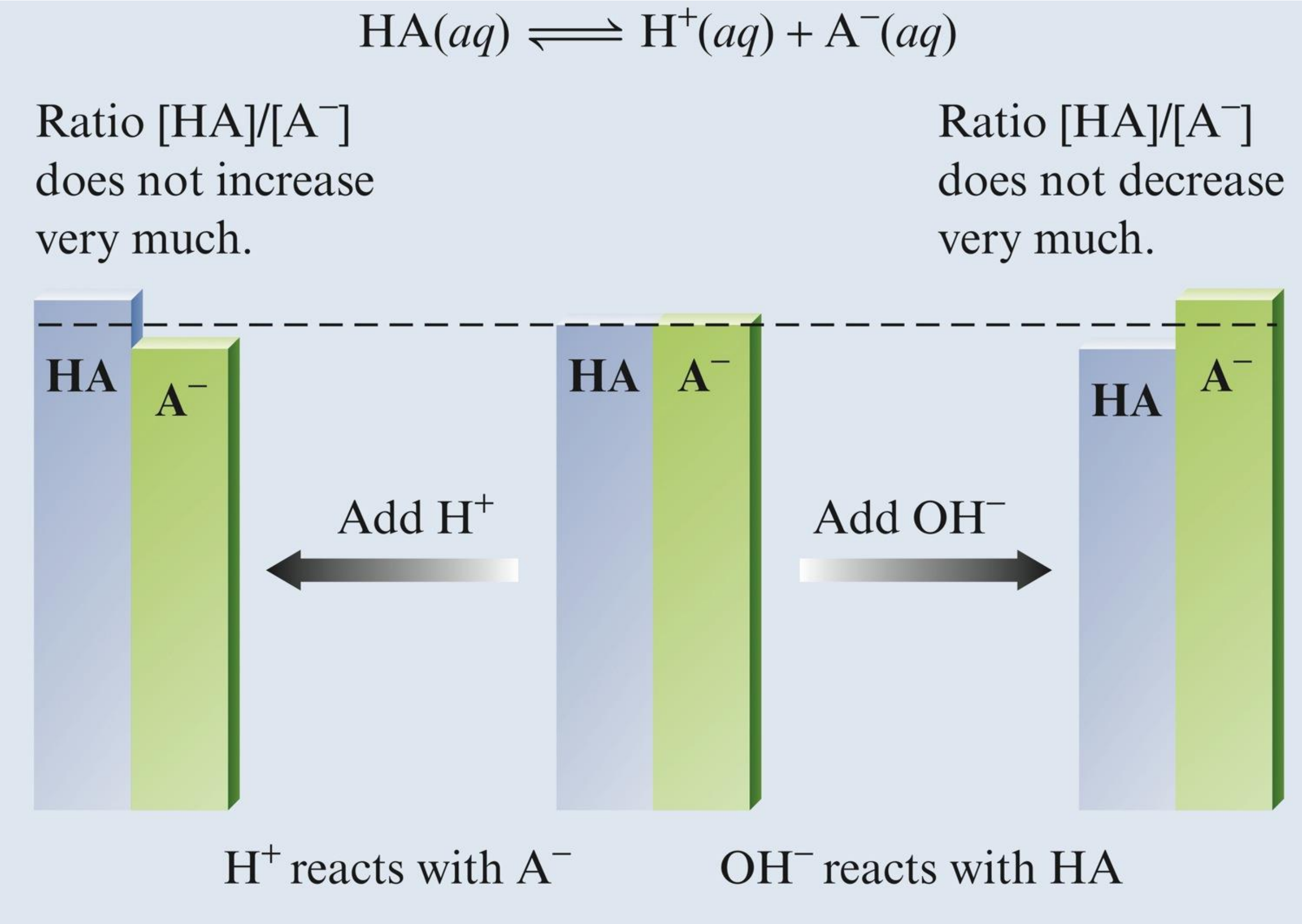
$\Delta\ pH = 7.00 - 12.08 = - 5.08$

Comment: compare the change in pH in both cases B and C.

BUFFERS RESIST ADDITION OF BASES AND ACIDS

THEY MAINTAIN THEIR pH.

Section 15.2
Buffered Solutions



$$HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$$

Ratio $[HA]/[A^-]$ does not increase very much.

Ratio $[HA]/[A^-]$ does not decrease very much.

H^+ reacts with A^-

OH^- reacts with HA

Effect of added H^+ or OH^- on a buffered system.

Weak base/conjugate acid buffer. (NH_3/NH_4^+), pH = ?

pOH = pK_b + log(acid/base) *Then* , pH = 14.0 - pOH

Example: NH_3/NH_4^+ Buffer ; $K_b = 1.8\text{x}10^{-5}$

Calculate the pH of a buffer of 0.25 M NH_3 and 0.40 M NH_4Cl?

$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$ *(strong electrolyte)*

0.40 M

$$NH_{3(aq)} + H_2O_{(aq)} \rightleftharpoons NH_4^+ + OH^-{}_{(aq)}$$ *(weak base)*

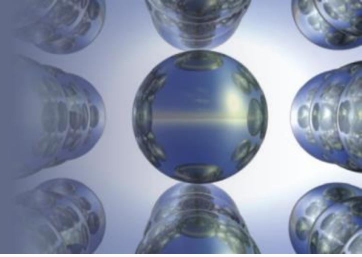
At eq.: (0.25M – x) x

$[OH^-] = (K_b)[NH_3]/[NH_4^+] = (1.8\text{x}10^{-5})(0.25)/(0.40) = 1.125\text{x}10^{-5}$ M

pOH = - log($1.125\text{x}10^{-5}$) = 4.95

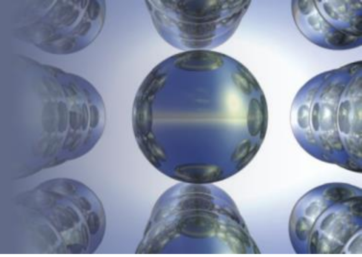
pH = 14.00 – 4.95 = 9.06 *(basic)*

Or Calculate $[H^+] = 1\text{x}10^{-14}/[OH^-]$ the pH



Buffer Solution Characteristics

- Buffers contain relatively large concentrations of a weak acid and corresponding conjugate base.
- Added H^+ reacts to completion with the weak base.
- Added OH^- reacts to completion with the weak acid.



Buffered Solution Characteristics

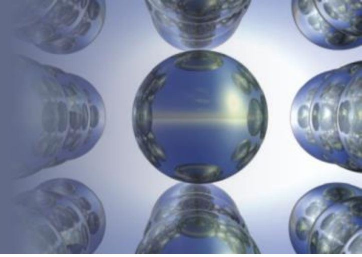
- The pH in the buffered solution is determined by the ratio of the concentrations of the weak acid and conjugate base. As long as this ratio remains virtually constant, the pH will remain virtually constant. This will be the case as long as the concentrations of the buffering materials (HA and A^- or B and BH^+) are large compared with amounts of H^+ or OH^- added.
- Buffer Capacity.
- Resist dilution.

Section 15.3
Buffering Capacity

- The amount of protons or hydroxide ions the buffer can absorb without a significant change in pH.
- Determined by the magnitudes of [HA] and [A^-].
- A buffer with large capacity contains large concentrations of the buffering components.

Section 15.3

Buffering Capacity



- Optimal buffering occurs when [HA] is equal to [A$^-$].
- It is for this condition that the ratio [A$^-$] / [HA] is most resistant to change when H$^+$ or OH$^-$ is added to the buffered solution.

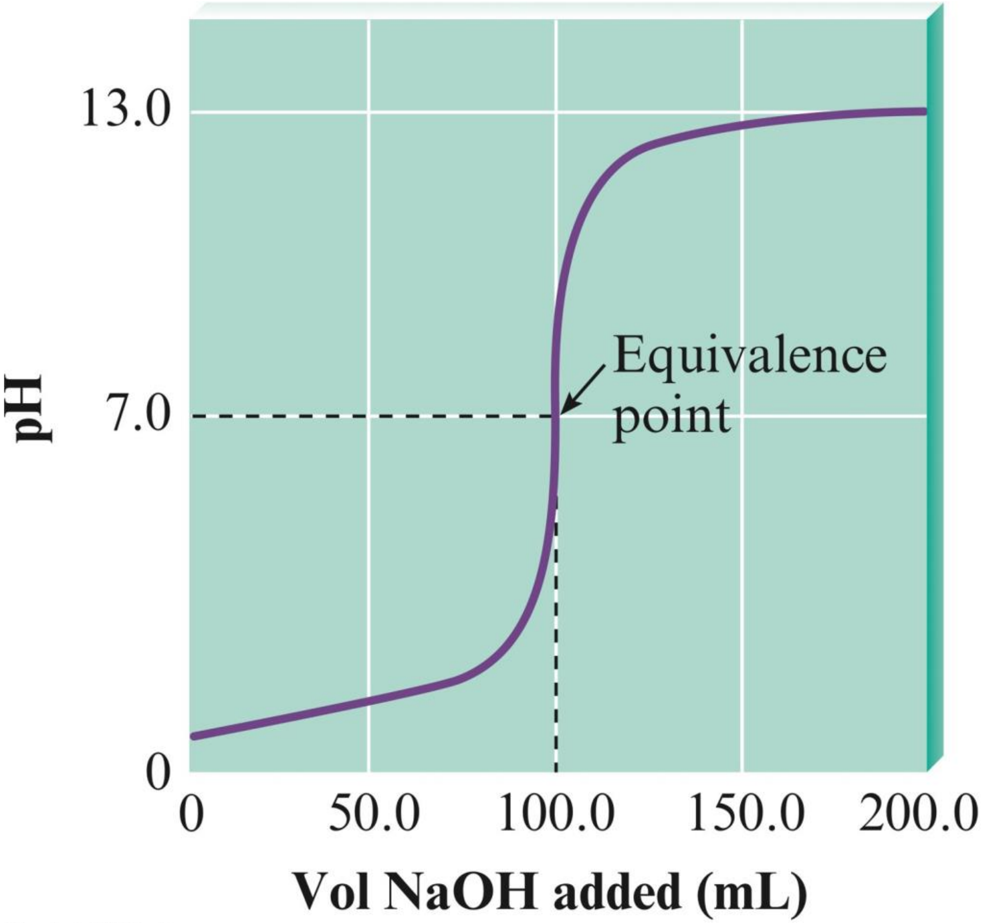
Choosing a Buffer

- pK_a of the weak acid to be used in the buffer should be as close as possible to the desired pH.

Titration Curve

- Plotting the pH of the solution being analyzed as a function of the amount of titrant added.
- Equivalence (Stoichiometric) Point – point in the titration when enough titrant has been added to react exactly with the substance in solution being titrated.

The pH Curve for the Titration of 50.0 mL of 0.200 *M* HNO_3 with 0.100 *M* NaOH



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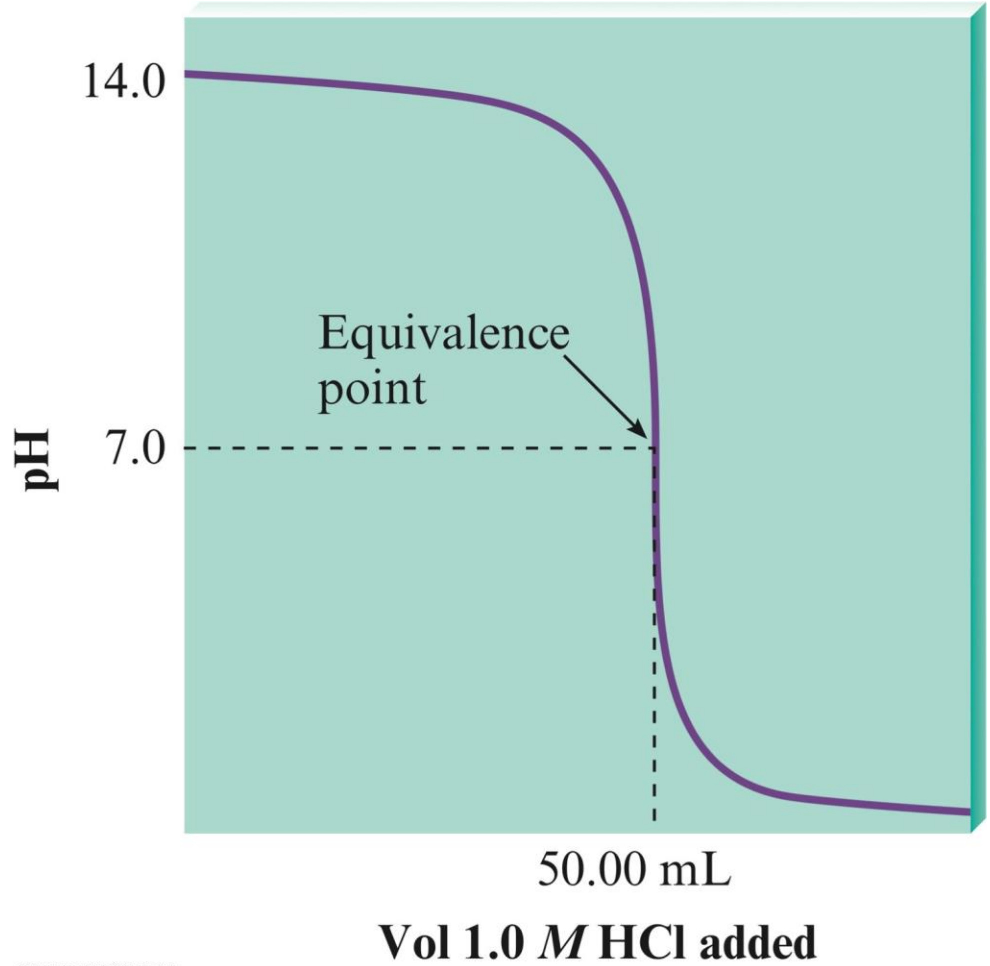
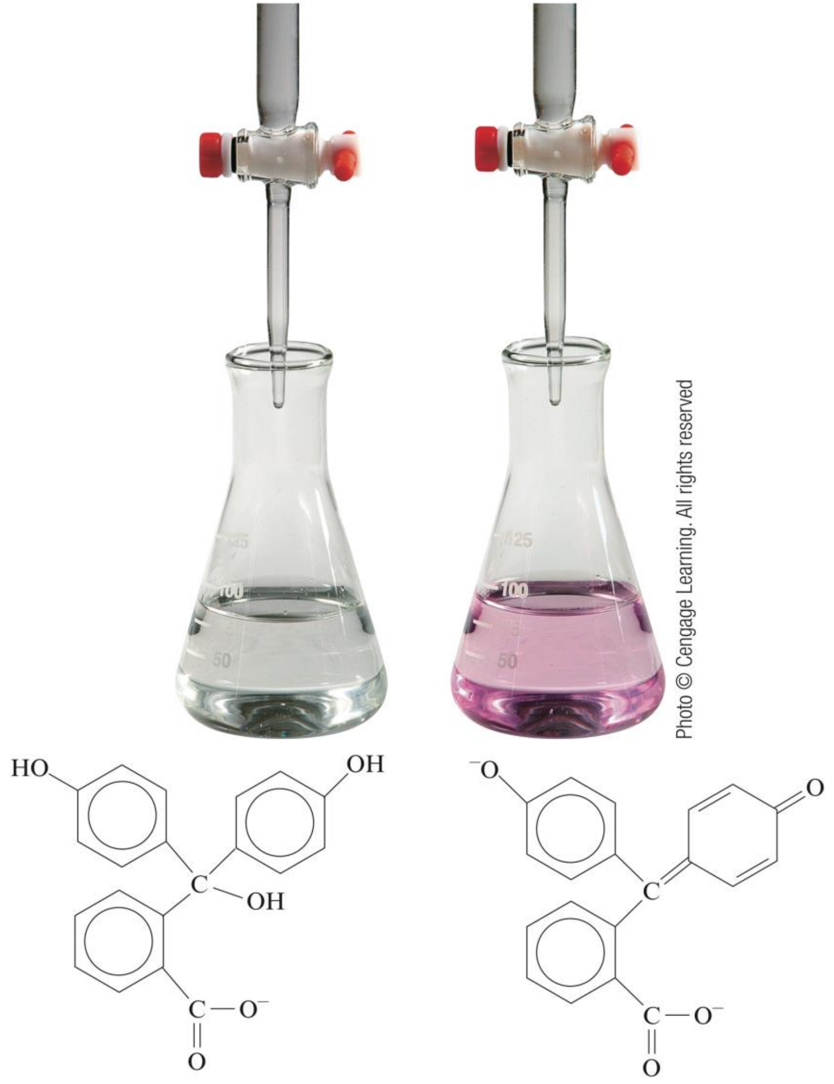
The pH Curve for the Titration of 100.0 mL of 0.50 *M* NaOH with 1.0 *M* HCl



The Acid and Base Forms of the Indicator Phenolphthalein



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Colorless acid form, HIn

Pink base form, In^-

The Methyl Orange Indicator is Yellow in Basic Solution and Red in Acidic Solution

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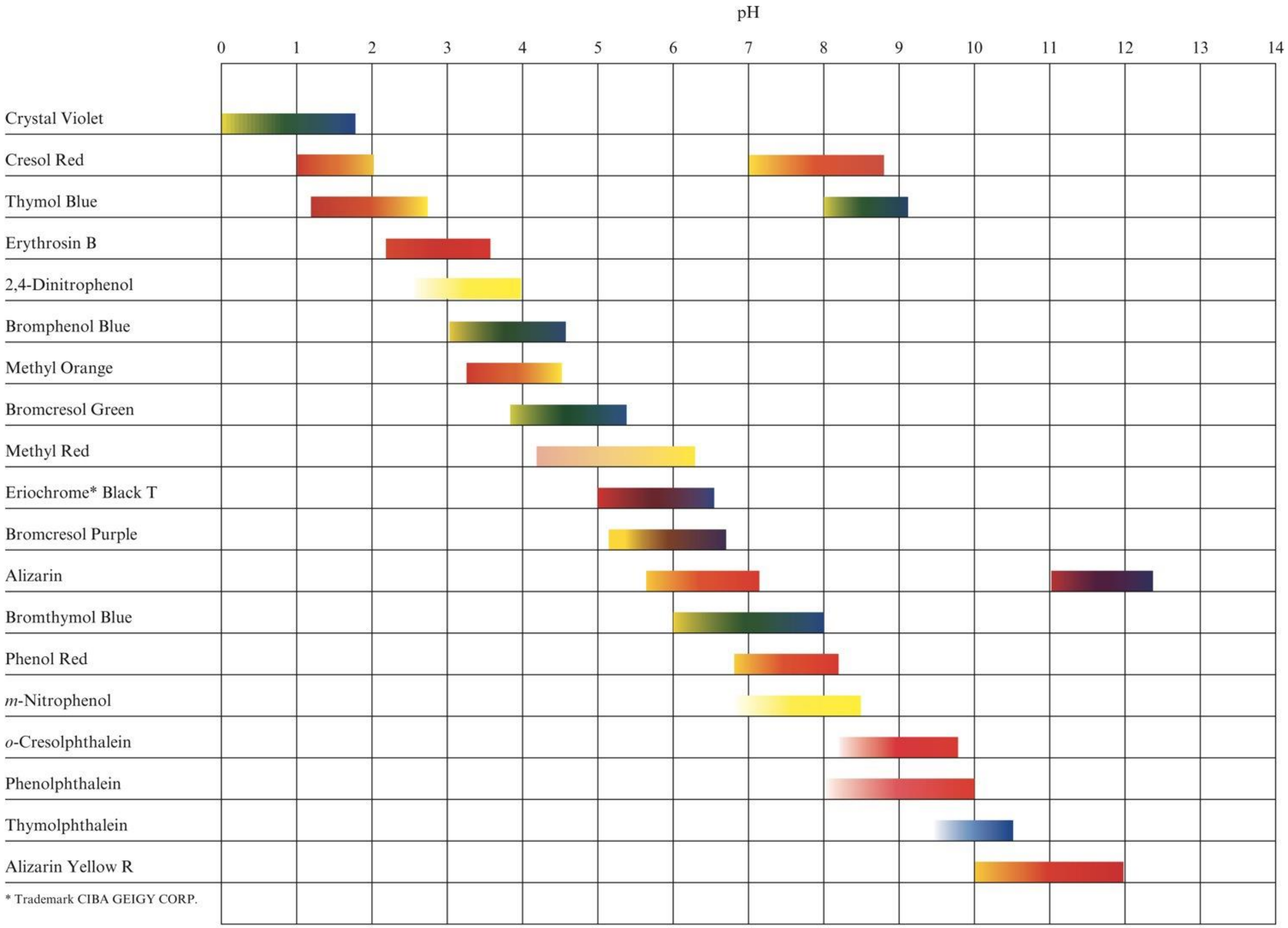
Useful pH Ranges for Several Common Indicators



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The pH ranges shown are approximate. Specific transition ranges depend on the indicator solvent chosen.