

## Chapter 15

### *Acid-Base Equilibria*

## Section 15.1

# *Solutions of Acids or Bases Containing a Common Ion*



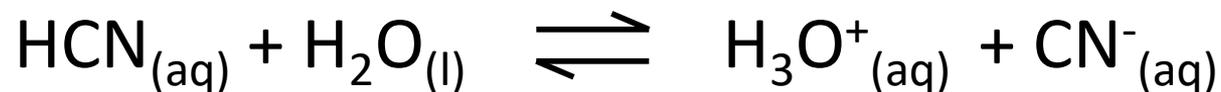
## Common Ion Effect

- 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.

## Section 15.1

### *Solutions of Acids or Bases Containing a Common Ion*

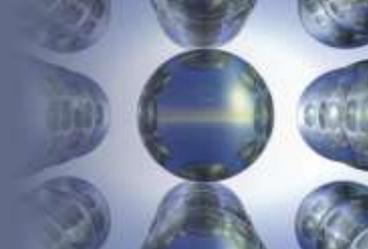
**Example:**



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

## Section 15.2

### *Buffered Solutions*



## Key Points about Buffered Solutions

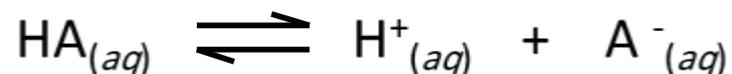
- Buffer solutions resist a change in pH.
- They are weak acids or weak bases containing a common ion.
- *OR* Buffers are mixtures of:
  - A weak acid and its conjugate base
  - OR* A weak base and its conjugate acid
- For a good buffer, both components should be of high concentrations.

## Section 15.2

### *Buffered Solutions*

■ Henderson–Hasselbalch Equation:

Consider the general weak acid equilibrium below:



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

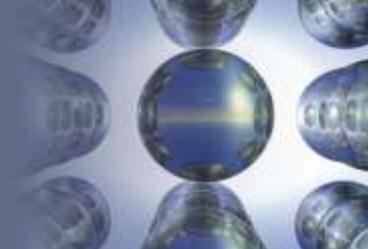
$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

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

## Section 15.2

### *Buffered Solutions*



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



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

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

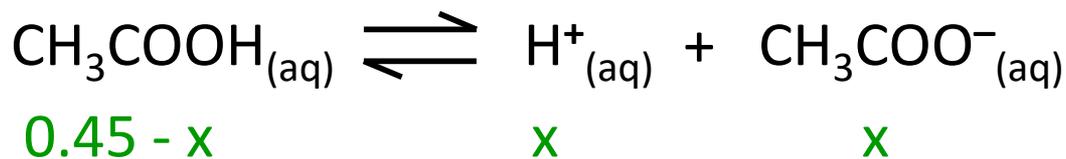
$$pOH = pK_b + \log \frac{[HB^+]}{[B]}$$

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

## Section 15.2

### *Buffered Solutions*

What is the pH of a buffer solution that is 0.45 M acetic acid ( $\text{HC}_2\text{H}_3\text{O}_2$ ) and 0.85 M sodium acetate ( $\text{NaC}_2\text{H}_3\text{O}_2$ )? The  $K_a$  for acetic acid is  $1.8 \times 10^{-5}$ .



$$K_a = [\text{H}^+][\text{CH}_3\text{COO}^-]/[\text{CH}_3\text{COOH}]$$

$$[\text{H}^+] = x \quad ; \quad [\text{CH}_3\text{COO}^-] = (x + 0.85 \text{ M}) \approx 0.85 \text{ M}$$

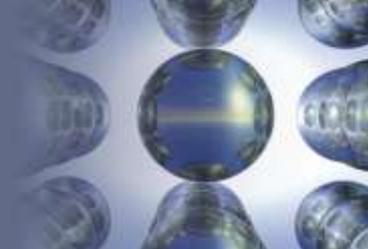
$$[\text{H}^+] = K_a([\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-])$$

$$= (1.8 \times 10^{-5})(0.45/0.85) = 9.53 \times 10^{-6}$$

$$\text{pH} = -\log(9.53 \times 10^{-6}) = 5.02 \quad \text{acidic}$$

## Section 15.2

### *Buffered Solutions*



Addition of strong acid to a buffer solution:

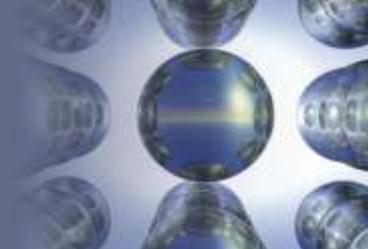
- A) Calculate the pH of a buffer solution that is 0.50 M acetic acid and 0.55 M sodium acetate?  $K_a = 1.75 \times 10^{-5}$ .
- B) Calculate the change in pH of the buffer in (A) when 0.480 g NaOH is added to 1 L of the buffer?
- C) Calculate the change in pH of the buffer in (A) when 0.480 g NaOH is added to 1 L of  $H_2O$ ? Comment on the results.

*Solution:*

$$\begin{aligned} A) \text{ pH} &= pK_a + \log \frac{[A^-]}{[HA]} = -\log(1.75 \times 10^{-5}) + \log 0.55/0.50 \\ &= +4.76 + 0.041 = 4.80 \end{aligned}$$

## Section 15.2

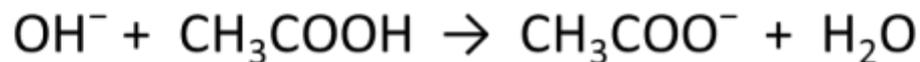
### *Buffered Solutions*



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  $[\text{CH}_3\text{COOH}]$  will decrease by 0.012 M and  $[\text{CH}_3\text{COO}^-]$  will increase by 0.012 M.



$$[\text{CH}_3\text{COOH}] = 0.50 - 0.012 = 0.488 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 0.55 + 0.012 = 0.562 \text{ M}$$

$$[\text{H}^+] = K_a \frac{[\text{HA}]}{[\text{A}]} = (1.75 \times 10^{-5}) \frac{0.488}{0.562} = 1.52 \times 10^{-5}$$

$$\text{pH} = -\log(1.52 \times 10^{-5}) = 4.82$$

$$\Delta \text{pH} = 4.80 - 4.82 = 0.020$$

## Section 15.2

### *Buffered Solutions*



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.

$[\text{OH}^-] = 0.012 \text{ M}$ , so,

$[\text{H}^+] = 1 \times 10^{-14} / 0.012 = 8.33 \times 10^{-13}$

$\text{pH} = -\log(8.33 \times 10^{-13}) = 12.08$

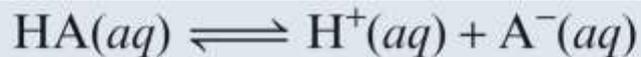
$\Delta \text{pH} = 7.00 - 12.08 = -5.08$

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

**BUFFERS RESIST ADDITION OF BASES AND ACIDS  
THEY MAINTAIN THEIR pH.**

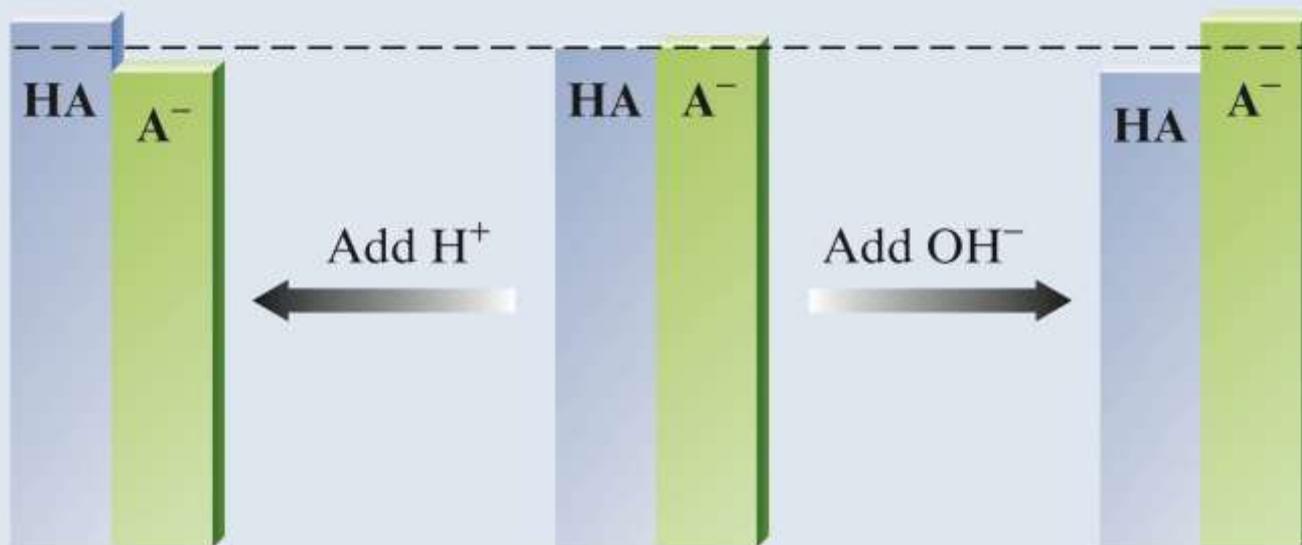
# Section 15.2

## *Buffered Solutions*



Ratio  $[\text{HA}]/[\text{A}^-]$   
does not increase  
very much.

Ratio  $[\text{HA}]/[\text{A}^-]$   
does not decrease  
very much.



$\text{H}^+$  reacts with  $\text{A}^-$

$\text{OH}^-$  reacts with  $\text{HA}$

*Effect of added  $\text{H}^+$  or  $\text{OH}^-$  on a buffered system.*

## Section 15.2

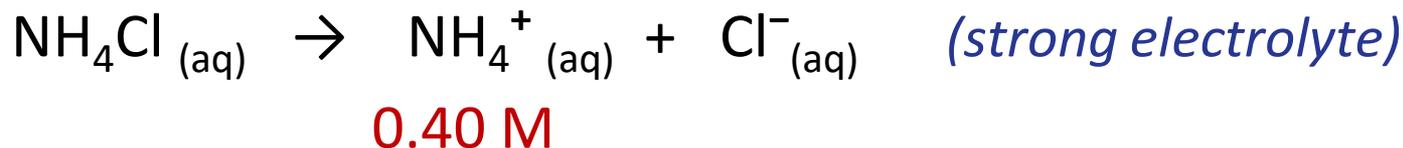
### *Buffered Solutions*

Weak base/conjugate acid buffer. ( $\text{NH}_3/\text{NH}_4^+$ ),  $\text{pH} = ?$

$\text{pOH} = \text{pK}_b + \log(\text{acid/base})$  *Then*,  $\text{pH} = 14.0 - \text{pOH}$

Example:  $\text{NH}_3/\text{NH}_4^+$  Buffer ;  $K_b = 1.8 \times 10^{-5}$

Calculate the pH of a buffer of 0.25 M  $\text{NH}_3$  and 0.40 M  $\text{NH}_4\text{Cl}$ ?



At eq.: **(0.25M - x)** **x**

$$[\text{OH}^-] = (K_b)[\text{NH}_3]/[\text{NH}_4^+] = (1.8 \times 10^{-5})(0.25)/(0.40) = 1.125 \times 10^{-5} \text{ M}$$

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

$$\text{pH} = 14.00 - 4.95 = 9.06 \quad (\text{basic})$$

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

## Section 15.2

### *Buffered Solutions*



#### Buffer Solution Characteristics

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

## Section 15.2

### *Buffered Solutions*



## 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 15.4

### *Titrations and pH Curves*



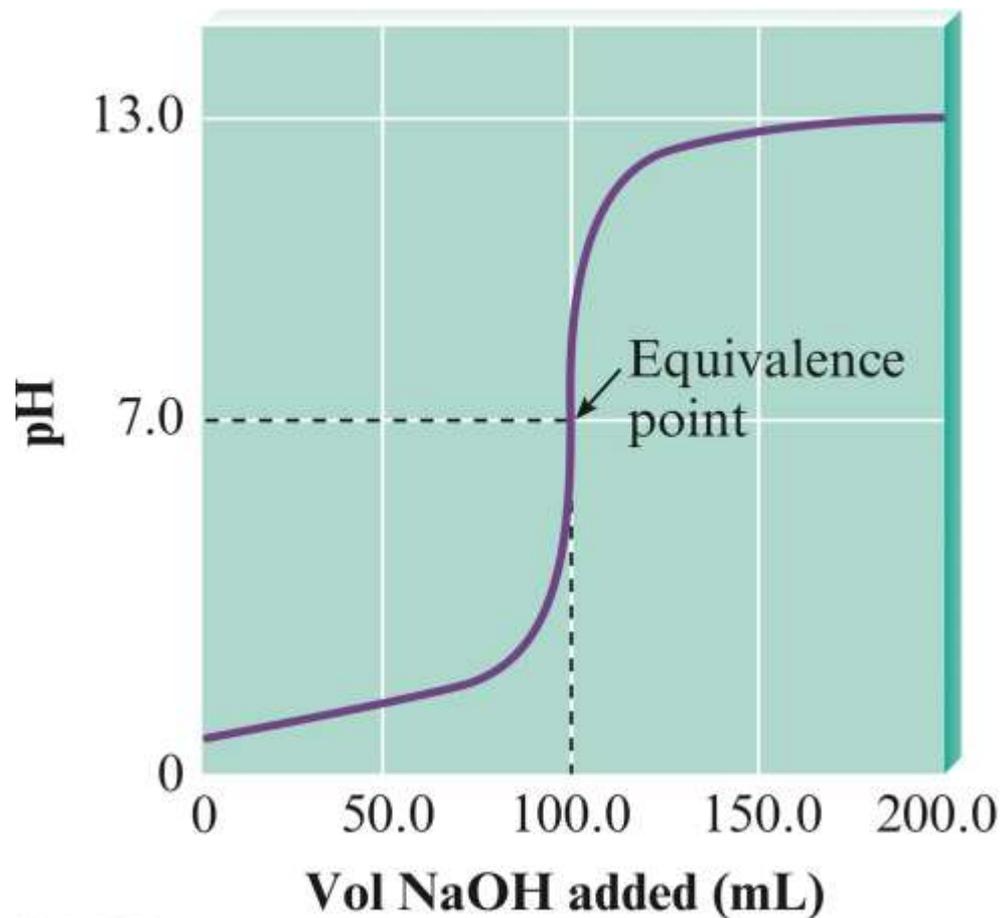
#### Titration Curve

- 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.

## Section 15.4

### *Titrations and pH Curves*

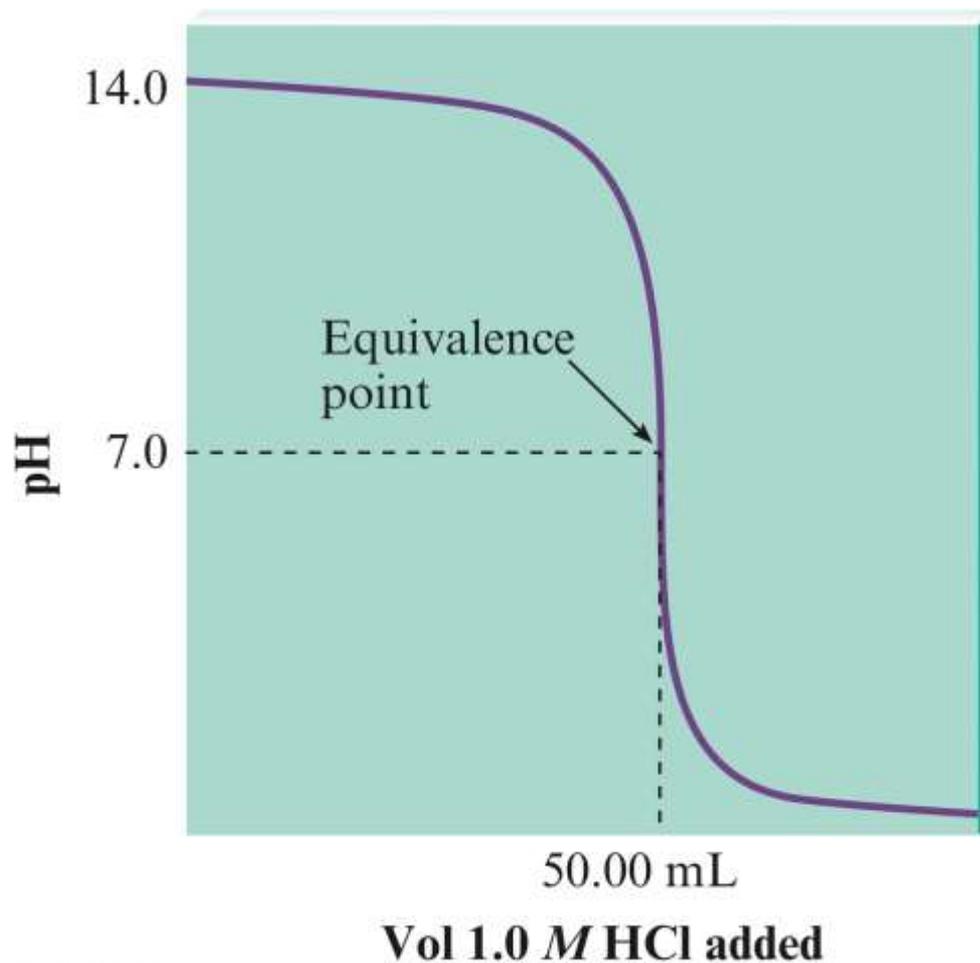
The pH Curve for the Titration of 50.0 mL of 0.200 M  $\text{HNO}_3$  with 0.100 M NaOH



# Section 15.4

## *Titrations and pH Curves*

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



## Section 15.5

### *Acid-Base Indicators*



- Marks the end point of a titration by changing color.
- The equivalence point is not necessarily the same as the end point (but they are ideally as close as possible).

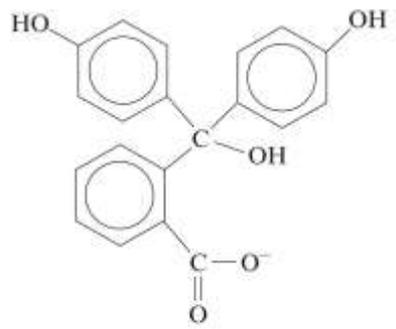
# Section 15.5

## *Acid-Base Indicators*

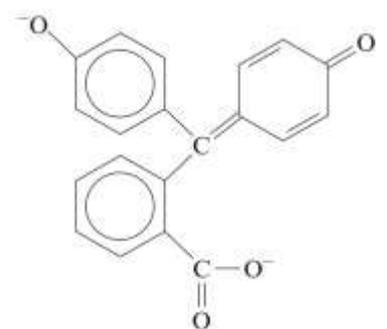
### The Acid and Base Forms of the Indicator Phenolphthalein



Photo © Cengage Learning. All rights reserved



Colorless acid form,  $\text{HIn}$



Pink base form,  $\text{In}^-$

# Section 15.5

## *Acid-Base Indicators*

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



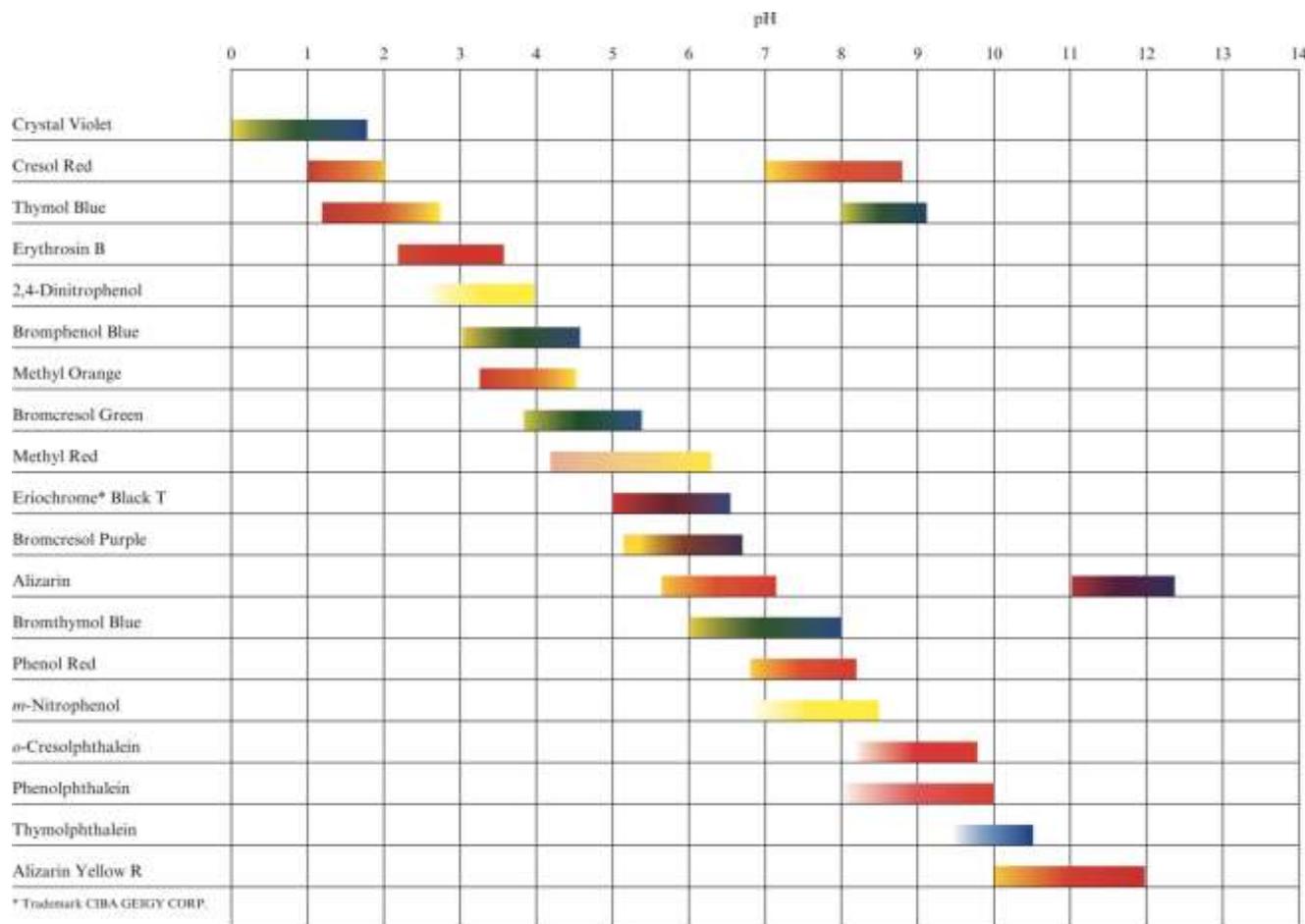
Photo © Cengage Learning. All rights reserved

# Section 15.5

## *Acid-Base Indicators*



### Useful pH Ranges for Several Common Indicators



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