# Chapter Fifteen

## Acids, Bases, and Acid–Base Equilibria
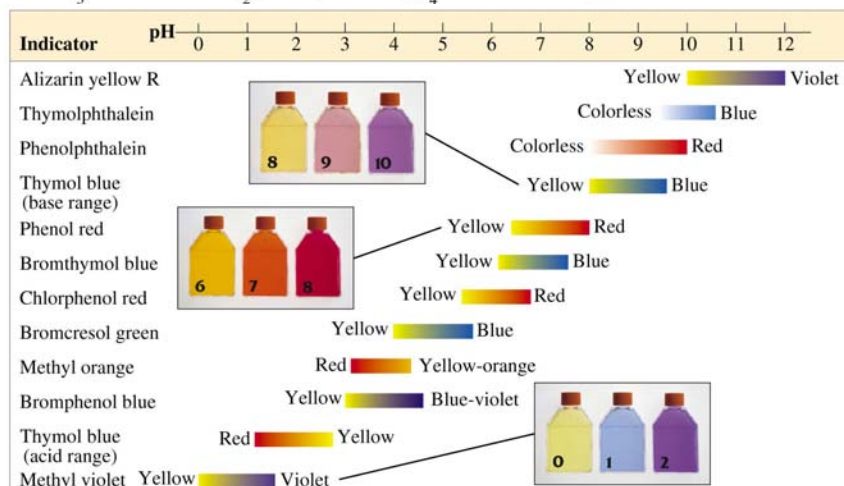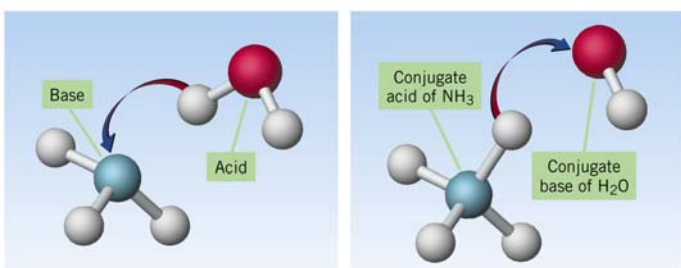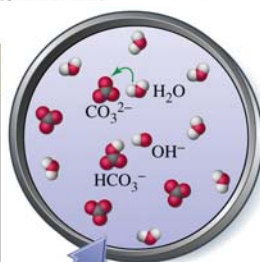
*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry
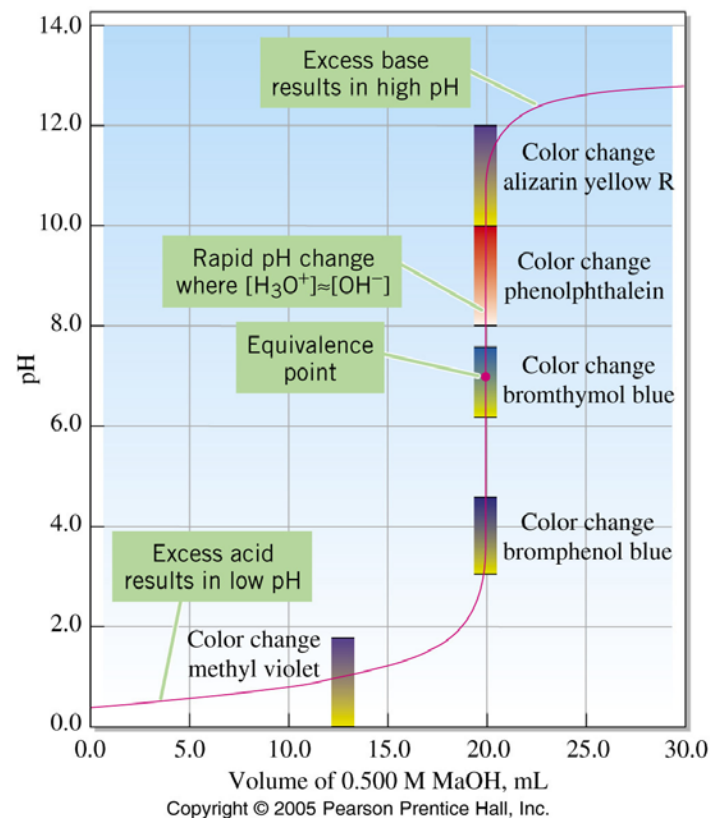
# The Brønsted–Lowry Theory

- Arrhenius theory: an acid forms $H^+$ in water; and a base forms $OH^-$ in water.

- But not all acid–base reactions involve water, and many bases ($NH_3$, carbonates) do not *contain* any $OH^-$.

- *Brønsted–Lowry* theory defines acids and bases in terms of proton ($H^+$) transfer.

- A ***Brønsted–Lowry acid*** is a ***proton donor***.

- A ***Brønsted–Lowry base*** is a ***proton acceptor***.

- The ***conjugate base*** of an acid is the acid minus the proton it has donated.

- The ***conjugate acid*** of a base is the base plus the accepted proton.

# Ionization of HCl
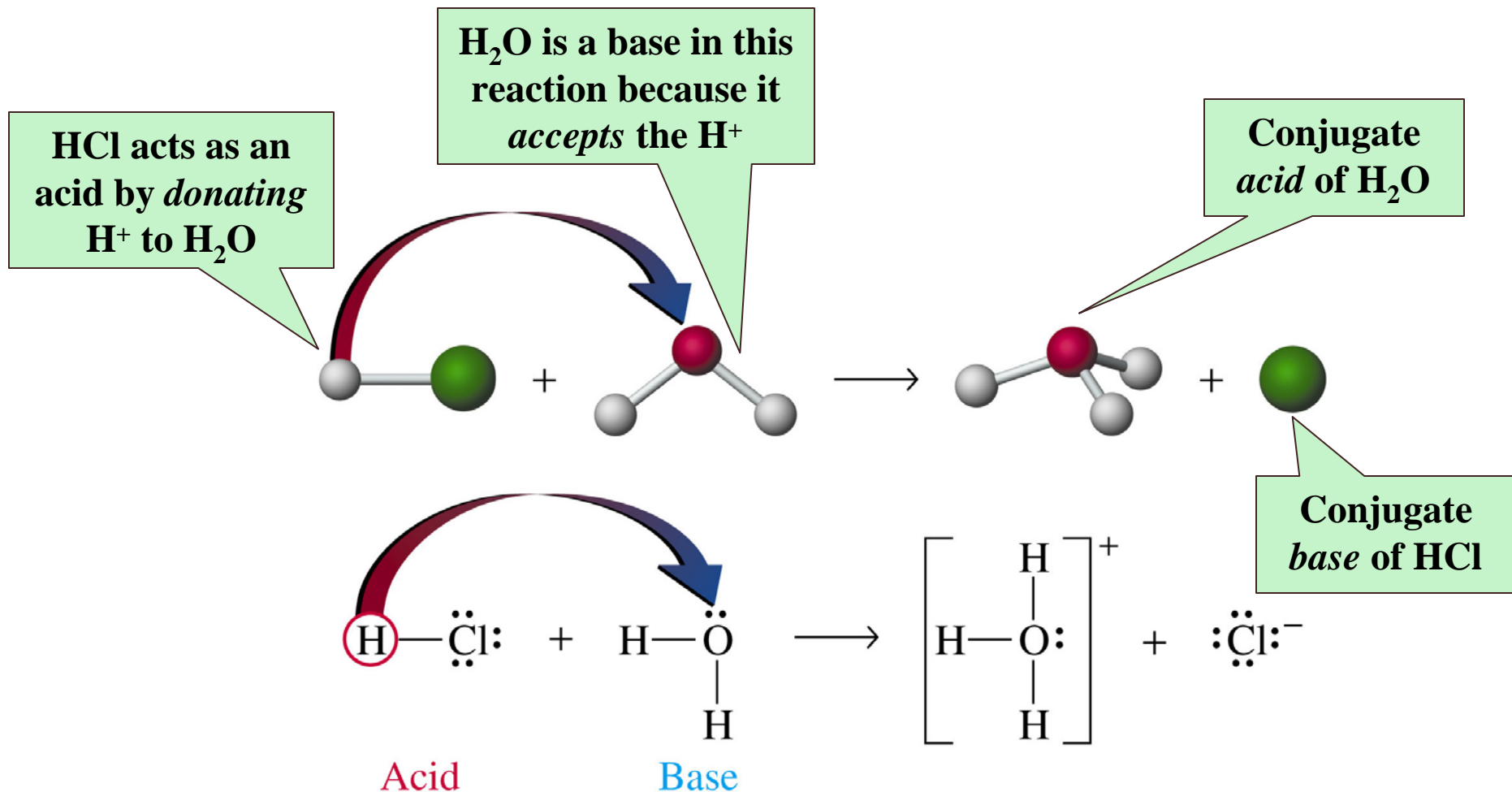
HCl acts as an acid by *donating* H+ to H2O

H2O is a base in this reaction because it *accepts* the H+

Conjugate *acid* of H2O

Conjugate *base* of HCl



Acid        Base

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# "Ionization" of Ammonia



Base

Acid

Conjugate
acid of $NH_3$

Conjugate
base of $H_2O$

$NH_3$ + $H_2O$ ⇌ $NH_4^+$ + $OH^-$

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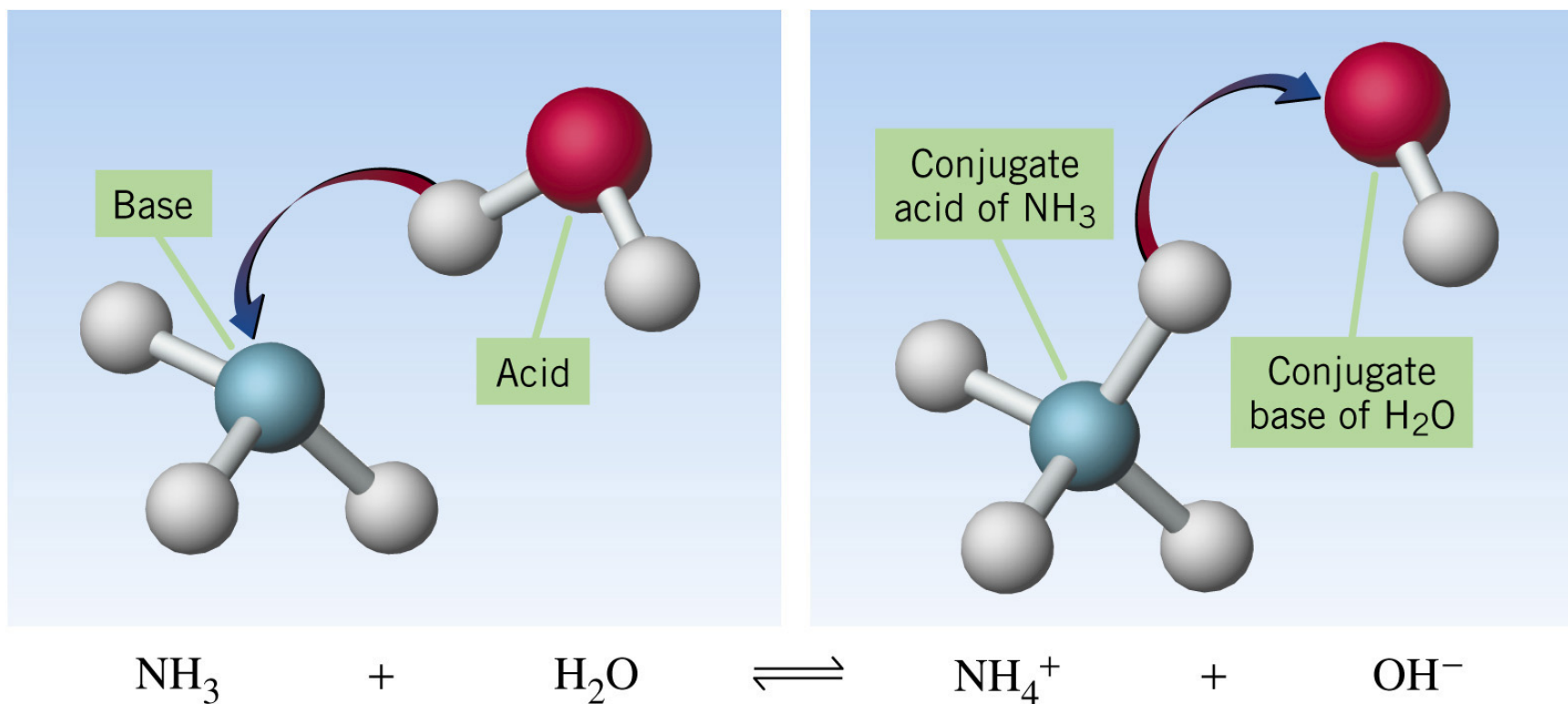
# Water Is Amphiprotic

$H_2O$ acts as an acid when it *donates* $H^+$, forming the conjugate base ___
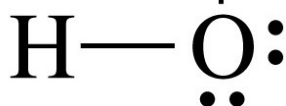
$H_2O$ acts as a base when it *accepts* $H^+$, forming the conjugate acid ___
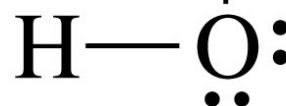
$H_2O$ as an acid

$H_2O$ as a base

Amphiprotic: Can act as either an acid or as a base

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# Example 15.1

Identify the Brønsted–Lowry acids and bases and their conjugates in:

(a) $H_2S + NH_3 \rightleftharpoons NH_4^+ + HS^-$

(b) $OH^- + H_2PO_4^- \rightleftharpoons H_2O + HPO_4^{2-}$

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# Acid–Base Equilibria

For equilibrium constant expressions, $K_a$ is used to represent the **acid ionization constant …**

… and $K_b$ is used to represent the **base ionization constant**

$$HA + H_2O \rightleftharpoons H^+ + A^- \qquad B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad\qquad K_b = \frac{[BH^+][OH^-]}{[B]}$$

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# $K_a$ and $K_b$

The equilibrium constant for a Brønsted acid is represented by $K_a$, and that for a base is represented by $K_b$.

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

Notice that H$_2$O is not included in either equilibrium expression.

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]}$$

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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# Strength of Conjugate Acid–Base Pairs

- A *stronger acid* can donate $H^+$ more readily than a weaker acid.

- The stronger an acid, the weaker is its conjugate base.

- The stronger a base, the weaker is its conjugate acid.

- An acid–base reaction is favored in the direction from the *stronger* member to the *weaker* member of each conjugate acid–base pair.
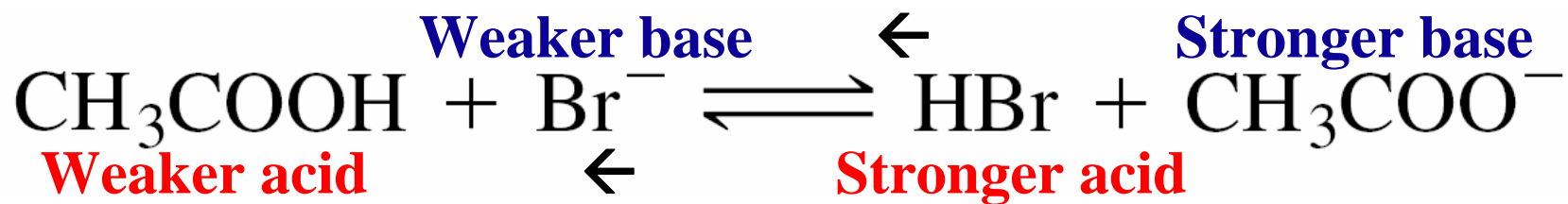
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## Table 15.1 Relative Strengths of Some Brønsted–Lowry Acids and Their Conjugate Bases

| Acid | Conjugate Base |
|---|---|
| HI    (hydroiodic acid) | $I^-$   (iodide ion) |
| HBr   (hydrobromic acid) | $Br^-$   (bromide ion) |
| HCl   (hydrochloric acid) | $Cl^-$   (chloride ion) |
| $H_2SO_4$   (sulfuric acid) | $HSO_4^-$   (hydrogen sulfate ion) |
| $HNO_3$   (nitric acid) | $NO_3^-$   (nitrate ion) |
| $H_3O^+$   (hydronium ion) | $H_2O$   (water) |
| $HSO_4^-$   (hydrogen sulfate ion) | $SO_4^{2-}$   (sulfate ion) |
| $HNO_2$   (nitrous acid) | $NO_2^-$   (nitrite ion) |
| HF   (hydrofluoric acid) | $F^-$   (fluoride ion) |
| $CH_3COOH$   (acetic acid) | $CH_3COO^-$   (acetate ion) |
| $H_2CO_3$   (carbonic acid) | $HCO_3^-$   (hydrogen carbonate ion) |
| $NH_4^+$   (ammonium ion) | $NH_3$   (ammonia) |
| $HCO_3^-$   (hydrogen carbonate ion) | $CO_3^{2-}$   (carbonate ion) |
| $H_2O$   (water) | $OH^-$   (hydroxide ion) |
| $CH_3OH$   (methanol) | $CH_3O^-$   (methoxide ion) |

The stronger the acid …

… the weaker the conjugate base.

… the weaker the conjugate acid.

And the stronger the base …

Increasing acid strength

Increasing base strength

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# Acid/Base Strength and Direction of Equilibrium

- In Table 15.1, HBr lies above $CH_3COOH$ in the acid column.

- Since HBr is a stronger acid than $CH_3COOH$, the equilibrium for the reaction:

**Weaker base** $\leftarrow$ **Stronger base**

$$CH_3COOH + Br^- \rightleftharpoons HBr + CH_3COO^-$$

**Weaker acid** $\leftarrow$ **Stronger acid**

lies to the *left*.

- We reach the same conclusion by comparing the strengths of the *bases* (right column of Table 15.1).

- $CH_3COO^-$ lies below $Br^-$ ; $CH_3COO^-$ is the stronger base:

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# Acid–Base Strength (cont'd)

$K_a$ values are used to compare the strengths of weak acids; $\uparrow K$, $\uparrow$ strength

For strong acids, water has a *leveling* effect; that is, when the strong acids are dissolved in water, they all completely ionize to the hydronium ion
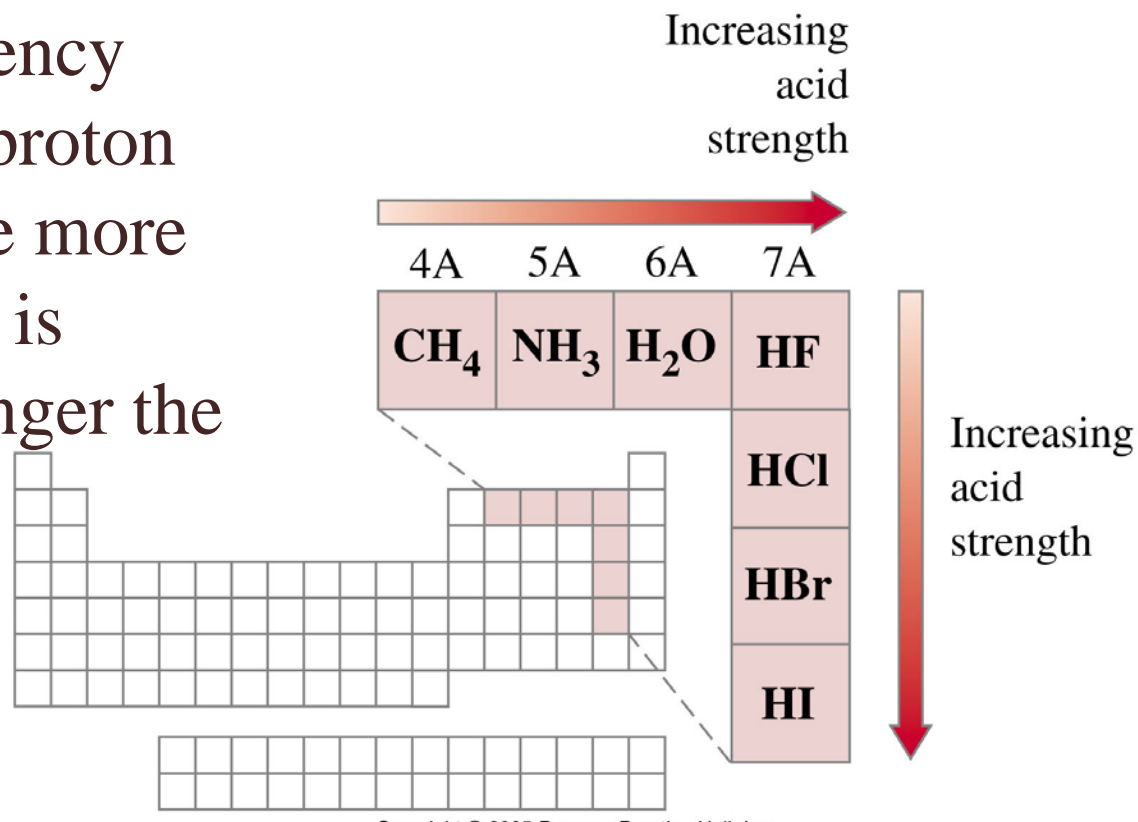
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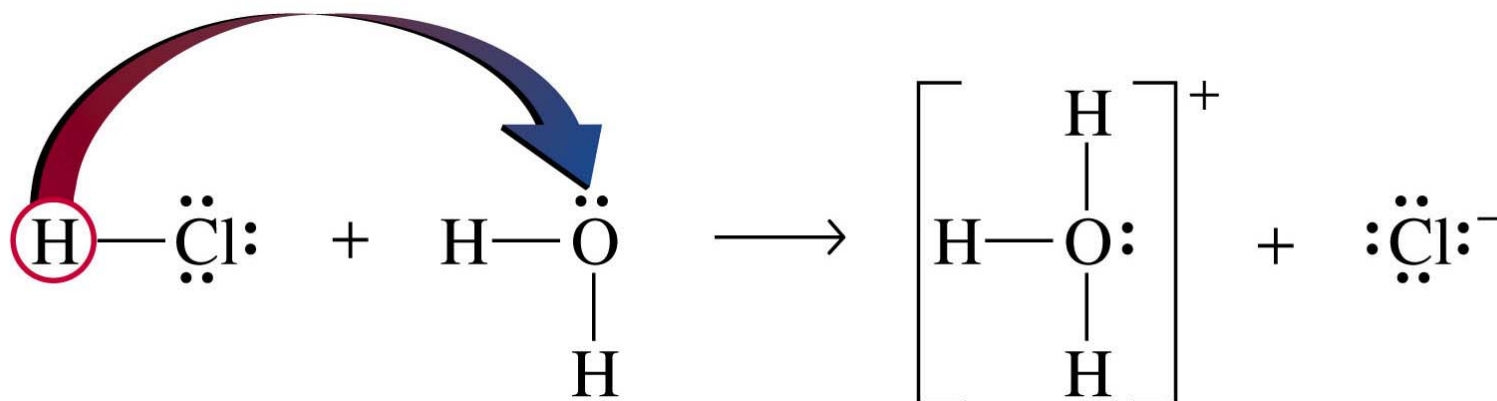
# Strong Acids

- The "strong" acids—HCl, HBr, HI, $HNO_3$, $H_2SO_4$, $HClO_4$—are considered "strong" because they ionize completely in water.

- The "strong" acids all appear above $H_3O^+$ in Table 15.1.

- The strong acids are *leveled* to the same strength—to that of $H_3O^+$—when they are placed in water.

HI
(hydroiodic acid)
HBr
(hydrobromic acid)
HCl
(hydrochloric acid)
$H_2SO_4$
(sulfuric acid)
$HNO_3$
(nitric acid)
$H_3O^+$
(hydronium ion)

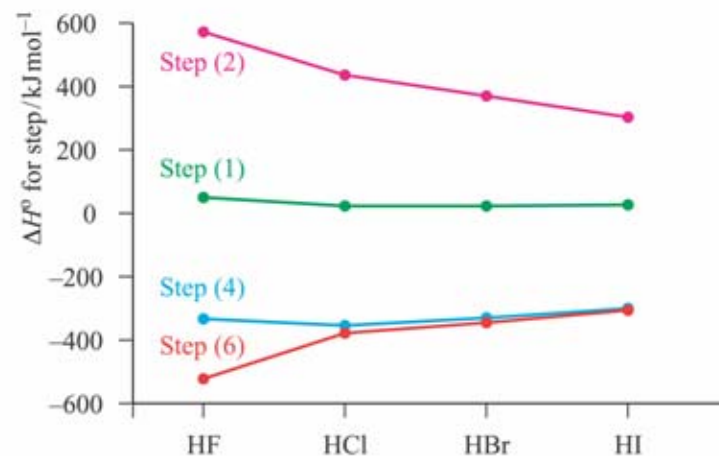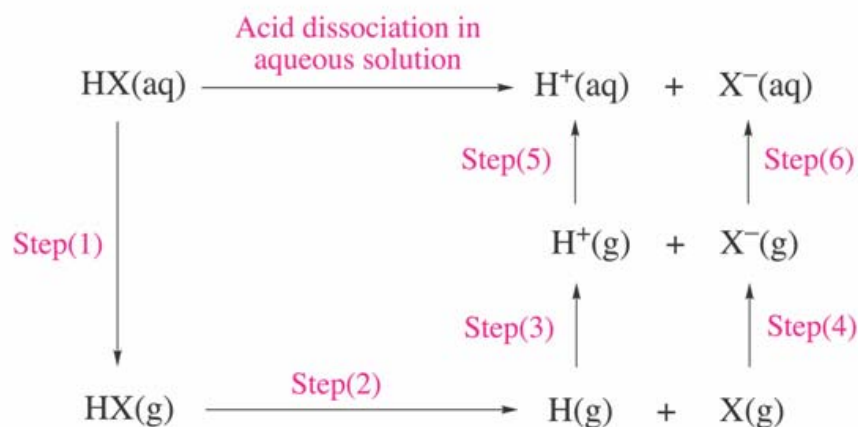*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Strengths of Binary Acids in a Periodic Group

The greater the tendency for the transfer of a proton from HX to $H_2O$, the more the *forward* reaction is favored and the stronger the acid



Increasing acid strength

|  | 4A | 5A | 6A | 7A |
|---|---|---|---|---|
|  | $CH_4$ | $NH_3$ | $H_2O$ | HF |
|  |  |  |  | HCl |
|  |  |  |  | HBr |
|  |  |  |  | HI |

Increasing acid strength

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# Strengths of Binary Acids in a Periodic Group



Energetics (Hess cycle) of the dissociation of a hydrogen halide, HX (X = F, Cl, Br, I), in aqueous solution

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# Strengths of Binary Acids in a Periodic Group

Bond-dissociation energy is inversely proportional to acid strength. The weaker the bond, the stronger the acid
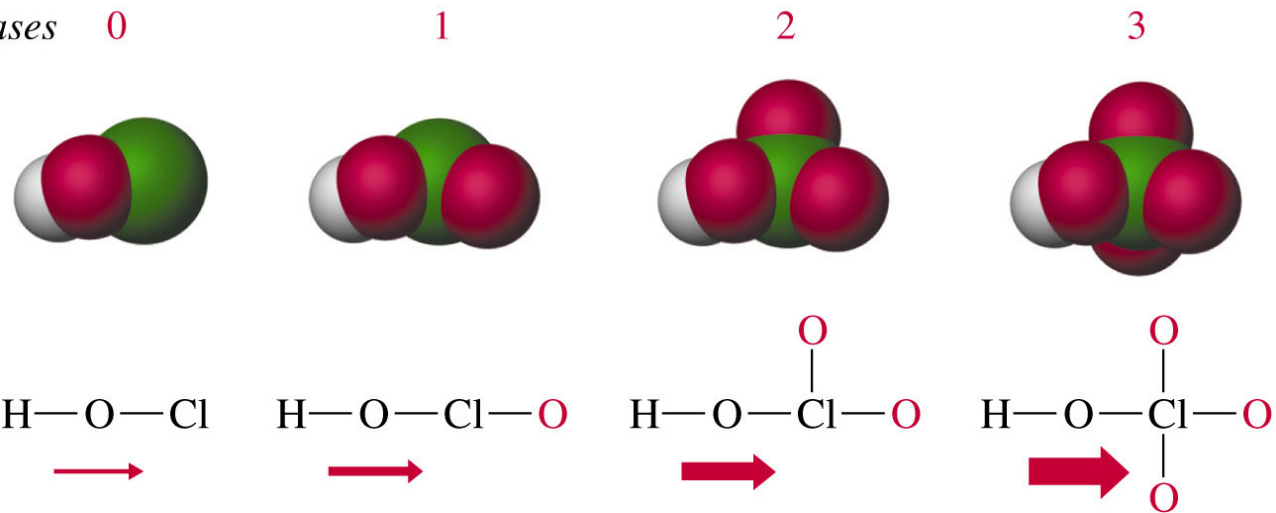
Anion radius is directly proportional to acid strength. The larger the resultant anion's radius, the stronger is the acid

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# Strength of Oxoacids

Acid strength *increases* with the electronegativity of the central atom, and with the *number* of terminal oxygen atoms.

Number of terminal O
atoms (red) increases          0                    1                    2                    3



$$H—O—Cl \quad H—O—Cl—O \quad H—O—\overset{\displaystyle O}{\underset{\displaystyle |}{Cl}}—O \quad H—O—\overset{\displaystyle O}{\underset{\displaystyle |}{\underset{\displaystyle O}{\overset{|}{Cl}}}}—O$$

Electron
withdrawal

Acid strength
increases        $K_a = 2.9 \times 10^{-8} \quad < \quad 1.1 \times 10^{-2} \quad < \quad \approx 1000 \quad < \quad \approx 10^8$

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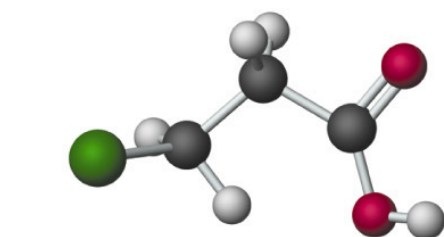# Strength of Carboxylic Acids

- *Carboxylic acids* all have the –COOH group in common.
- Differences in acid strength come from differences in the R group attached to the carboxyl group.
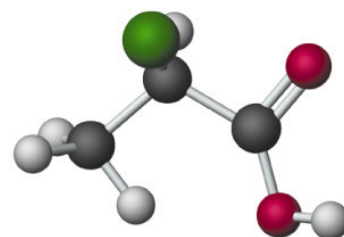- In general, the more that electronegative atoms appear in the R group, the stronger is the acid.
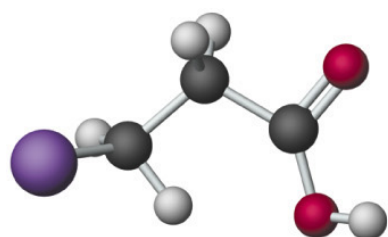
I—$CH_2CH_2COOH$
3-Iodopropanoic acid
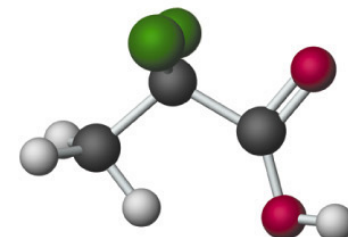$K_a = 8.3 \times 10^{-5}$  <  

Cl—$CH_2CH_2COOH$
3-Chloropropanoic acid
$K_a = 1.0 \times 10^{-4}$  <  

$CH_3CHClOOH$
2-Chloropropanoic acid
$K_a = 1.4 \times 10^{-3}$  <  

$CH_3CCl_2COOH$
2,2-Dichloropropanoic acid
$K_a = 8.7 \times 10^{-3}$

*Increasing acid strength*

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Example 15.2

Select the stronger acid in each pair:

**(a)** nitrous acid, $HNO_2$, and nitric acid, $HNO_3$

**(b)** $Cl_3CCOOH$ and $BrCH_2COOH$

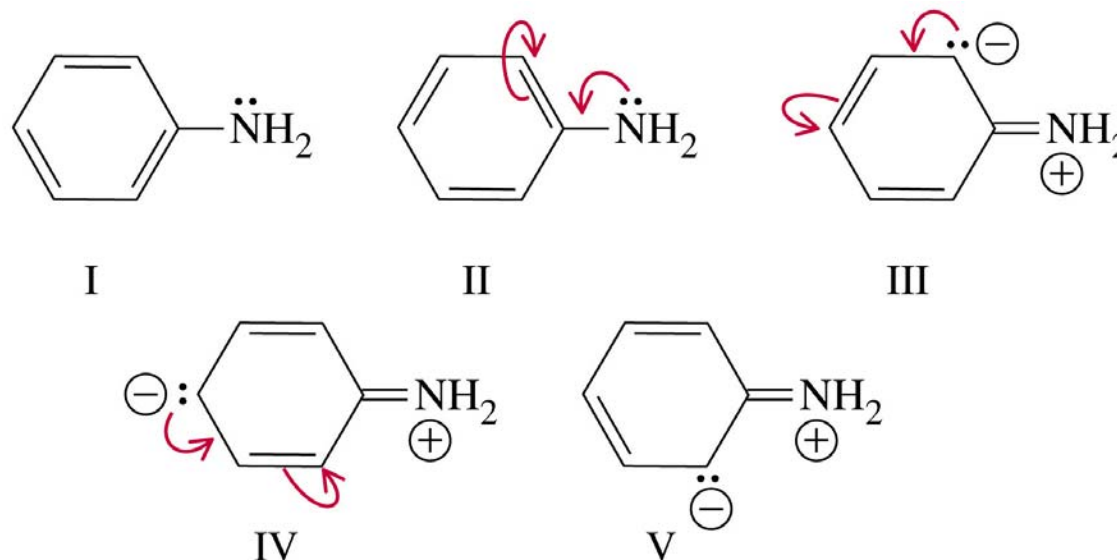*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Strengths of Amines as Bases

- Aromatic amines are much weaker bases than aliphatic amines.

- This is due in part to the fact that the $\pi$ electrons in the benzene ring of an aromatic molecule are *delocalized* and can involve the nitrogen atom's lone-pair electrons in the resonance hybrid.

- As a result, the lone-pair electrons are much less likely to accept a proton.

- Electron-withdrawing groups on the ring further diminish the basicity of aromatic amines relative to aniline.

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Strengths of Amines as Bases

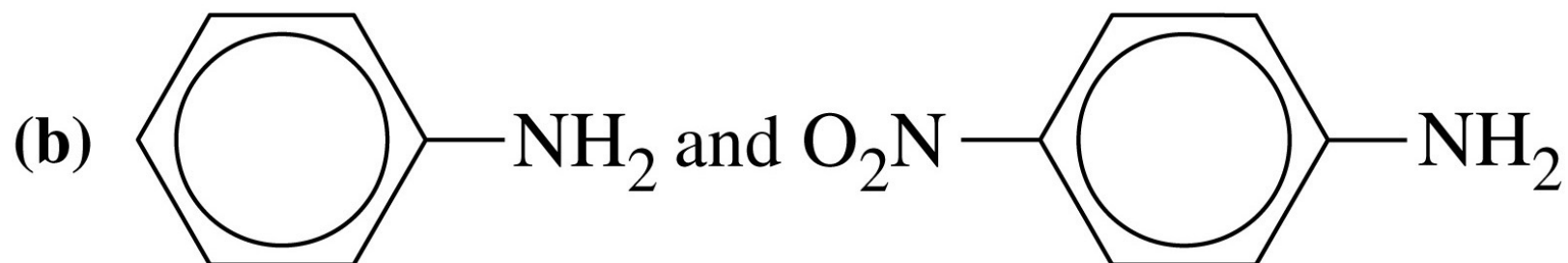Aromatic amines are much weaker bases than aliphatic amines

$\pi$ electrons in the benzene ring of an aromatic molecule are *delocalized* and can involve the N's lone-pair electrons in the resonance hybrid
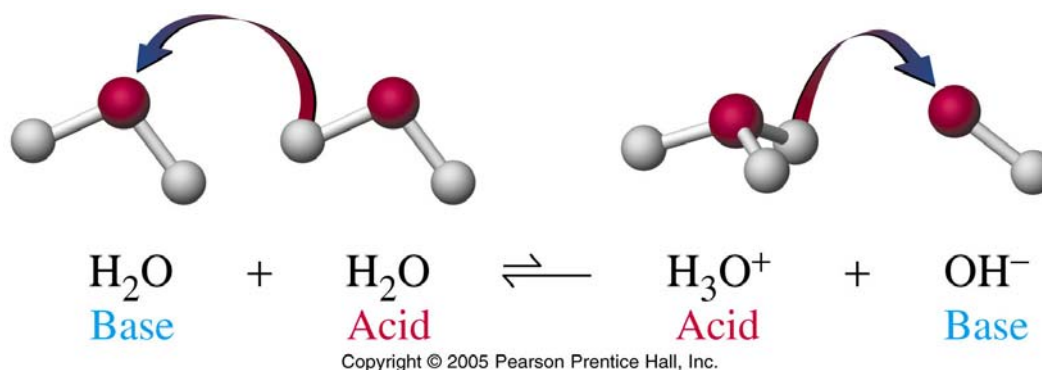


I          II          III

IV          V

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# Example 15.3

Select the weaker base in each pair:

(a) $HOCH_2CH_2NH_2$ and $CH_3CH_2NH_2$

(b) —$NH_2$ and $O_2N$——$NH_2$

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# Self-Ionization of Water

- Even pure water conducts some electricity. This is due to the fact that water self-ionizes:

$$H_2O \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O^+ \quad + \quad OH^-$$

Base          Acid                    Acid           Base

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- The equilibrium constant for this process is called the *ion product of water* ($K_w$).
- At 25 °C, $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$
- This equilibrium constant is very important because it applies to *all aqueous solutions*—acids, bases, salts, and nonelectrolytes—not just to pure water.

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# The pH Scale

- Concentration of $H_3O^+$ can vary over a wide range in aqueous solution, from about 10 M to about $10^{-14}$ M.

- A more convenient expression for $H_3O^+$ is **pH**.

$$pH = -\log [H_3O^+] \quad \text{and so} \quad [H_3O^+] = 10^{-pH}$$
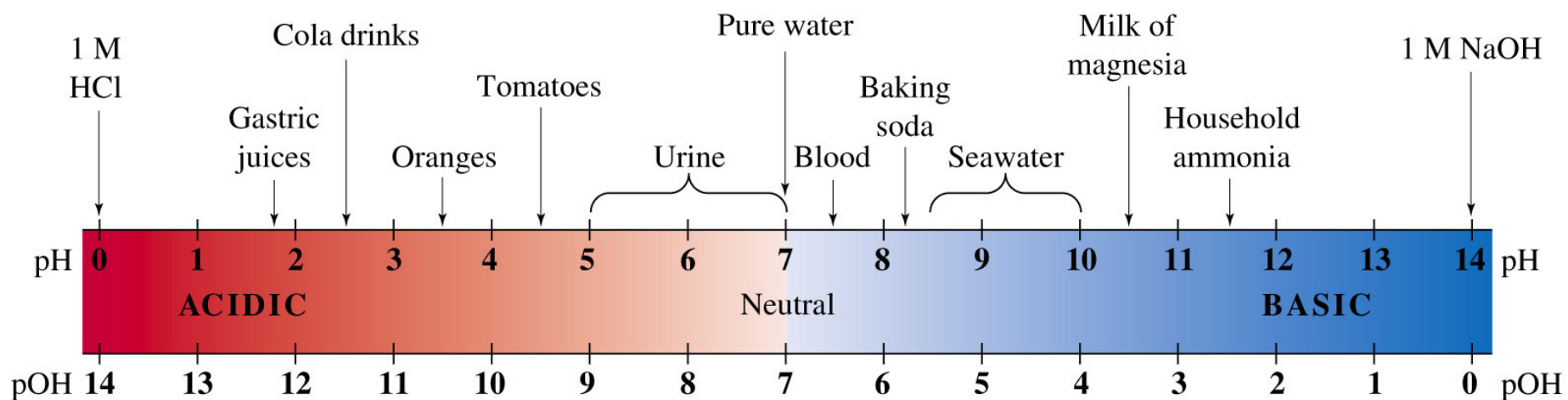
- The "negative logarithm" function of pH is so useful that it has been applied to other species and constants.

$$\textbf{pOH} = -\log [OH^-] \quad \text{and so} \quad [OH^-] = 10^{-pOH}$$

$$\textbf{p}K_w = -\log K_w$$

- At 25 °C, $pK_w = 14.00$

- $pK_w = pH + pOH = 14.00$

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# The pH Scale

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# Example 15.4

By the method suggested in Figure below, a student determines the pH of milk of magnesia, a suspension of solid magnesium hydroxide in its saturated aqueous solution, and obtains a value of 10.52. What is the molarity of $Mg(OH)_2$ in its saturated aqueous solution? The suspended, undissolved $Mg(OH)_2(s)$ does not affect the measurement.

# Example 15.5

# A Conceptual Example

Is the solution $1.0 \times 10^{-8}$ M HCl acidic, basic, or neutral?



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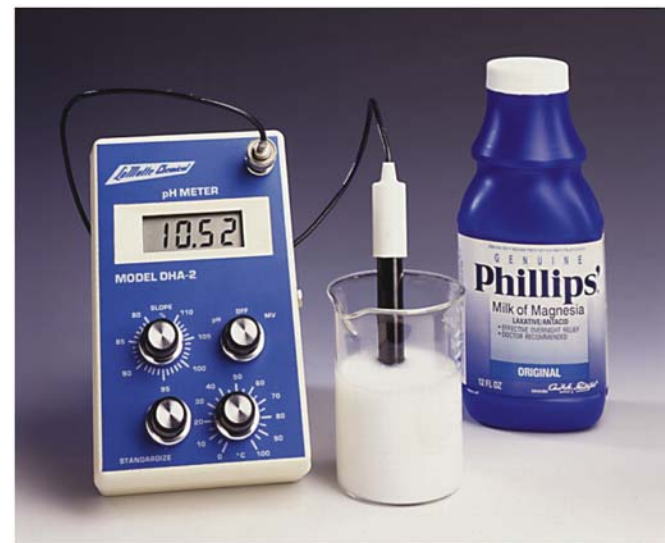
# Equilibrium in Solutions of Weak Acids and Weak Bases

These calculations are similar to the equilibrium calculations performed in Chapter 14.

1. An equation is written for the reversible reaction.
2. Data are organized, often in an ICE format.
3. Changes that occur in establishing equilibrium are assessed.
4. Simplifying assumptions are examined (the "5% rule"- negligible ionization = $x < 5\%$ $M_{acid}$); (Also, check if $M_{acid}/K_a > 100$).
5. Equilibrium concentrations, equilibrium constant, etc. are calculated.

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## Table 15.2 Ionization Constants of Some Weak Acids and Weak Bases in Water at 25 °C

| | Ionization Equilibrium | Ionization Constant, $K$ | p$K$ |
|---|---|---|---|
| **Inorganic Acids** | | $K_a =$ | |
| Chlorous acid | $HClO_2 + H_2O \rightleftharpoons H_3O^+ + ClO_2^-$ | $1.1 \times 10^{-2}$ | 1.96 |
| Nitrous acid | $HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$ | $7.2 \times 10^{-4}$ | 3.14 |
| Hydrofluoric acid | $HF + H_2O \rightleftharpoons H_3O^+ + F^-$ | $6.6 \times 10^{-4}$ | 3.18 |
| Hypochlorous acid | $HOCl + H_2O \rightleftharpoons H_3O^+ + OCl^-$ | $2.9 \times 10^{-8}$ | 7.54 |
| Hypobromous acid | $HOBr + H_2O \rightleftharpoons H_3O^+ + OBr^-$ | $2.5 \times 10^{-9}$ | 8.60 |
| Hydrocyanic acid | $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-$ | $6.2 \times 10^{-10}$ | 9.21 |
| **Carboxylic Acids** | | $K_a =$ | |
| Chloroacetic acid | $CH_2ClCOOH + H_2O \rightleftharpoons H_3O^+ + CH_2ClCOO^-$ | $1.4 \times 10^{-3}$ | 2.85 |
| Formic acid | $HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$ | $1.8 \times 10^{-4}$ | 3.74 |
| Benzoic acid | $C_6H_5COOH + H_2O \rightleftharpoons H_3O^+ + C_6H_5COO^-$ | $6.3 \times 10^{-5}$ | 4.20 |
| Acetic acid | $CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$ | $1.8 \times 10^{-5}$ | 4.74 |
| **Inorganic Bases** | | $K_b =$ | |
| Ammonia | $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$ | $1.8 \times 10^{-5}$ | 4.74 |
| Hydrazine | $H_2NNH_2 + H_2O \rightleftharpoons H_2NNH_3^+ + OH^-$ | $8.5 \times 10^{-7}$ | 6.07 |
| Hydroxylamine | $HONH_2 + H_2O \rightleftharpoons HONH_3^+ + OH^-$ | $9.1 \times 10^{-9}$ | 8.04 |
| **Amines** | | $K_b =$ | |
| Dimethylamine | $(CH_3)_2NH + H_2O \rightleftharpoons (CH_3)_2NH_2^+ + OH^-$ | $5.9 \times 10^{-4}$ | 3.23 |
| Ethylamine | $CH_3CH_2NH_2 + H_2O \rightleftharpoons CH_3CH_2NH_3^+ + OH^-$ | $4.3 \times 10^{-4}$ | 3.37 |
| Methylamine | $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$ | $4.2 \times 10^{-4}$ | 3.38 |
| Pyridine | $C_5H_5N + H_2O \rightleftharpoons C_5H_5NH^+ + OH^-$ | $1.5 \times 10^{-9}$ | 8.82 |
| Aniline | $C_6H_5NH_2 + H_2O \rightleftharpoons C_6H_5NH_3^+ + OH^-$ | $7.4 \times 10^{-10}$ | 9.13 |

# Example 15.6

Ordinary vinegar is approximately 1 M $CH_3COOH$ and as shown in Figure 15.6, it has a pH of about 2.4. Calculate the expected pH of 1.00 M $CH_3COOH(aq)$, and show that the calculated and measured pH values are in good agreement.

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## Example 15.7

What is the pH of 0.00200 M ClCH$_2$COOH(aq)?
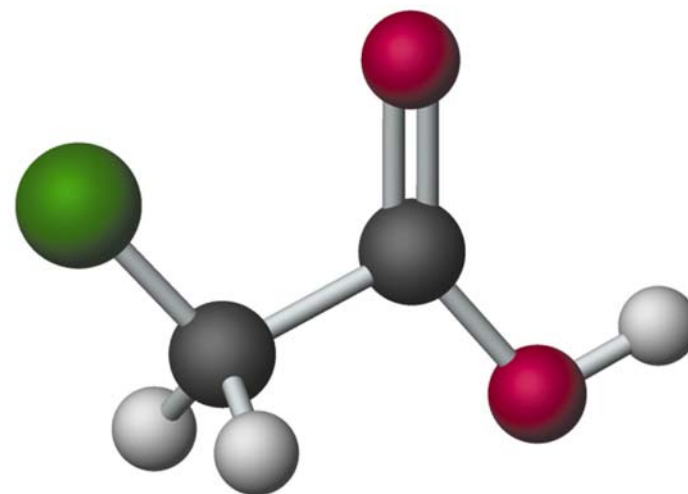
## Example 15.10    A Conceptual Example

Without doing detailed calculations, indicate which solution has the greater [H$_3$O$^+$], 0.030 M HCl or 0.050 M CH$_3$COOH.

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# Polyprotic Acids

- A *monoprotic acid* has one ionizable H atom per molecule.
- A *polyprotic acid* has more than one ionizable H atom per molecule.
  - Sulfuric acid, $H_2SO_4$      Diprotic
  - Carbonic acid, $H_2CO_3$      Diprotic
  - Phosphoric acid, $H_3PO_4$      Triprotic
- The protons of a polyprotic acid dissociate in steps, each step having a value of $K_a$.
- Values of $K_a$ decrease successively for a given polyprotic acid. $K_{a1} > K_{a2} > K_{a3}$, etc.
- Simplifying assumptions may be made in determining the concentration of various species from polyprotic acids.

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# Example 15.11

Calculate the following concentrations in an aqueous solution that is 5.0 M $H_3PO_4$:

**(a)** $[H_3O^+]$    **(b)** $[H_2PO_4^-]$    **(c)** $[HPO_4^{2-}]$    **(d)** $[PO_4^{3-}]$

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# Ions as Acids and Bases

- HCl is a ***strong*** acid, therefore $Cl^-$ is so weakly basic in water that a solution of chloride ions (such as NaCl) is virtually neutral.

- Acetic acid, $CH_3COOH$, is a ***weak*** acid, so acetate ion, $CH_3COO^-$, is significantly *basic* in water.

- A solution of sodium acetate (which dissociates completely into sodium and acetate ions in water) is therefore slightly basic:

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + \mathbf{OH^-}$$
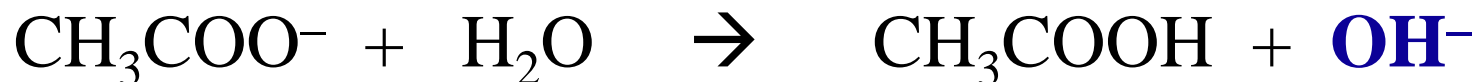
# Carbonate Ion as a Base



A carbonate ion accepts a proton from water, leaving behind an OH⁻ and making the solution *basic*.

$CO_3^{2-}$

$H_2O$

$OH^-$

$HCO_3^-$

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry
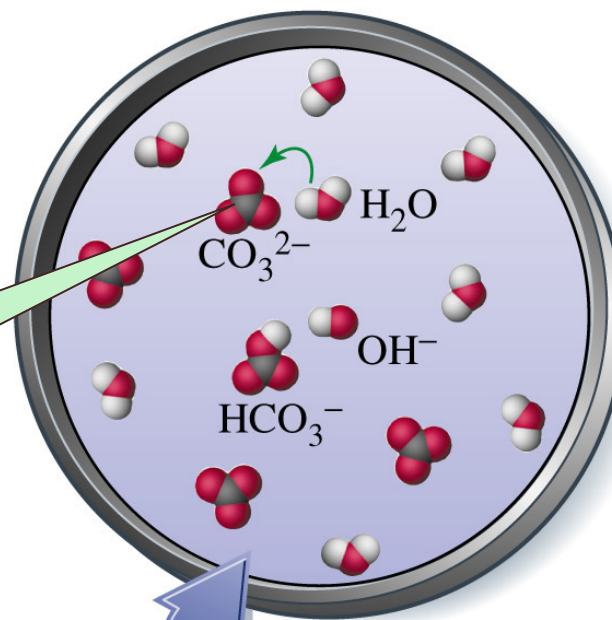
# Ions as Acids and Bases (cont'd)

- Salts of strong acids and strong bases form *neutral* solutions: $NaCl$, $KNO_3$

- Salts of weak acids and strong bases form *basic* solutions: $KNO_2$, $NaClO$

- Salts of strong acids and weak bases form *acidic* solutions: $NH_4NO_3$

- Salts of weak acids and weak bases form solutions that may be acidic, neutral, or basic; it depends on the relative strengths of the cations and the anions: $NH_4NO_2$, $CH_3COONH_4$.

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

Chapter Fifteen

# Example 15.13          A Conceptual Example

**(a)** Is $NH_4I(aq)$ acidic, basic, or neutral? **(b)** What conclusion can you draw from Figure 15.8d about the equilibrium constants for the hydrolysis reactions in $CH_3COONH_4(aq)$?



(a)          NaCl(aq)          (b)          $CH_3COONa(aq)$          (c)          $NH_4Cl(aq)$          (d)          $CH_3COONH_4(aq)$
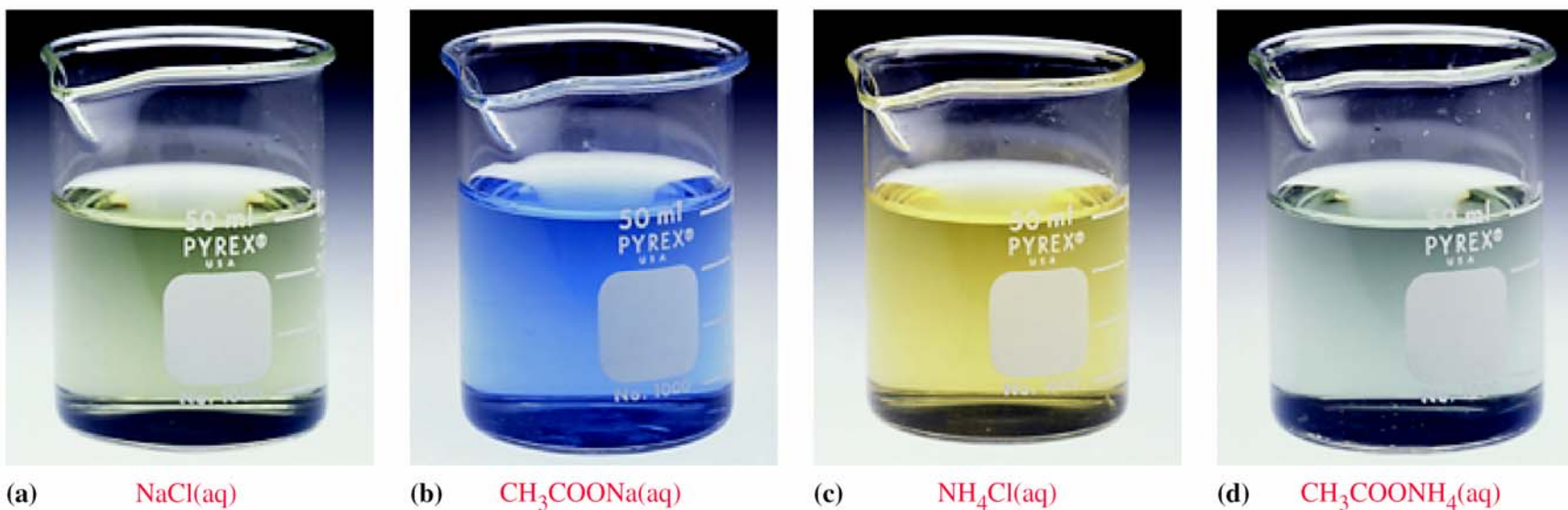
▲ FIGURE 15.8     The pH of aqueous solutions of salts

Each solution contains a few drops of bromthymol blue indicator, which is yellow in solutions having a pH below 7, green in solutions for which the pH is 7, and blue in solutions having a pH above 7. (a) A solution of sodium chloride is neutral. (b) A solution of sodium acetate is basic. (c) A solution of ammonium chloride is acidic. (d) A solution of ammonium acetate is neutral.

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Ions as Acids and Bases (cont'd)

- In order to make *quantitative* predictions of pH of a salt solution, we need an equilibrium constant for the hydrolysis reaction.

- The relationship between $K_a$ and $K_b$ of a conjugate acid–base pair is:

$$K_a \times K_b = K_w$$

- If instead we have values of $pK_a$ or $pK_b$:

$$pK_a + pK_b = pK_w = 14.00 \text{ (at 25 °C)}$$

# Ionization Constant Relationships

$pK_w$ is the negative logarithm of $K_w$ and at 25 °C is equal to 14.00

$$pK_w = pH + pOH = 14.00$$

$$K_w = [H^+][OH^-] = 1 \times 10^{-14}$$

For conjugate acid–base pairs …

$$K_w = (K_a)(K_b) = 1 \times 10^{-14}$$

EOS

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# Acid–Base Equilibrium Calculations

These calculations are similar to the equilibrium calculations performed in Chapter 14

The "5% rule" says that, for these equilibrium calculations to work properly, the acid must not dissociate more than 5% in water

EOS

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# The Common Ion Effect

- Consider a solution of acetic acid.
- If we add acetate ion as a second solute (i.e., sodium acetate), the pH of the solution *increases*:

When a salt supplies $CH_3COO^-$, equilibrium shifts to the *left*.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+ + CH_3COO^-$$
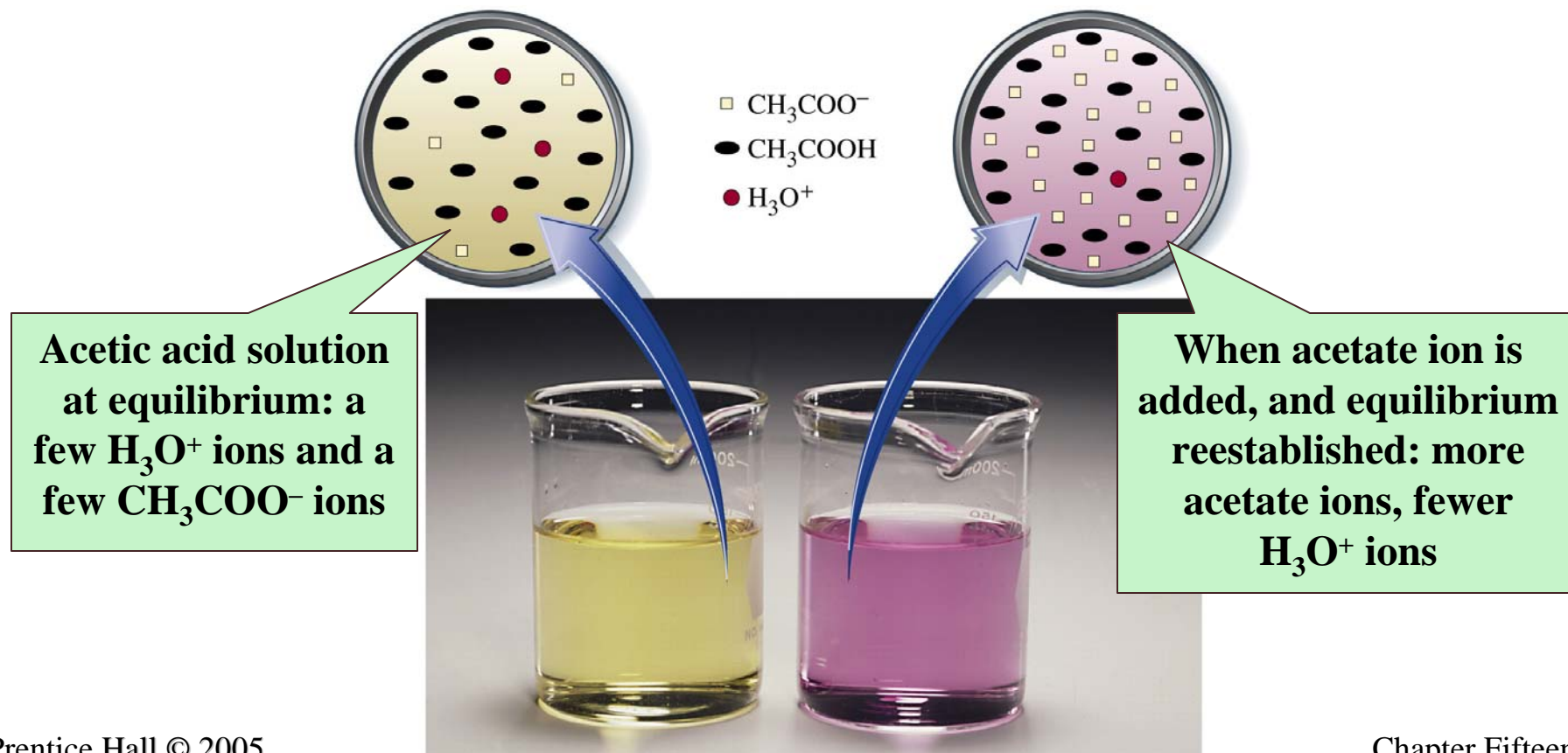
Acid        Base        Acid        Base
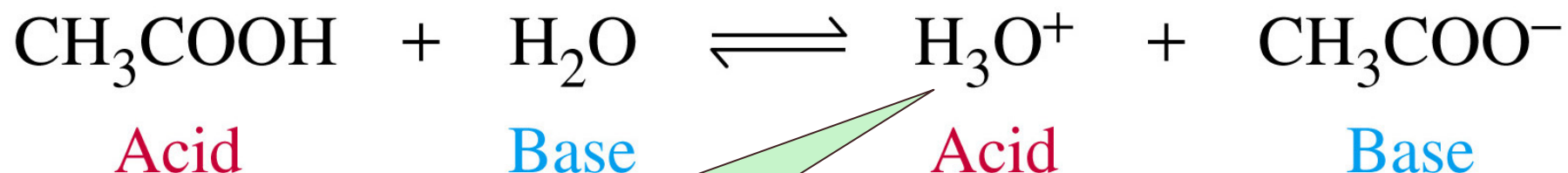
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LeChâtelier's principle: What happens to $[H_3O^+]$ when the equilibrium shifts to the left?

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# The Common Ion Effect (cont'd)

The *common ion effect* is the suppression of the ionization of a weak acid or a weak base by the presence of a common ion from a strong electrolyte.



□ $CH_3COO^-$
● $CH_3COOH$
● $H_3O^+$

**Acetic acid solution at equilibrium: a few $H_3O^+$ ions and a few $CH_3COO^-$ ions**

**When acetate ion is added, and equilibrium reestablished: more acetate ions, fewer $H_3O^+$ ions**

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# Buffer Solutions

A **buffer solution** is a solution that changes pH only slightly when small amounts of a strong acid or a strong base are added
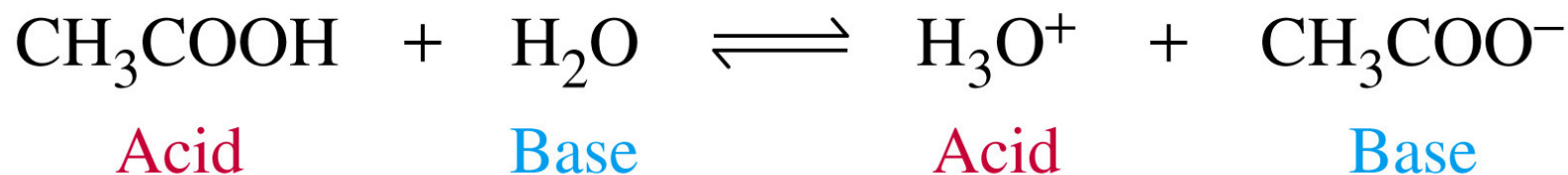
A buffer is prepared by mixing a weak acid with its salt (conjugate base) or by mixing a weak base with its salt (conjugate acid) in aqueous solution

Example: HF (hydrofluoric acid) and NaF (sodium fluoride)

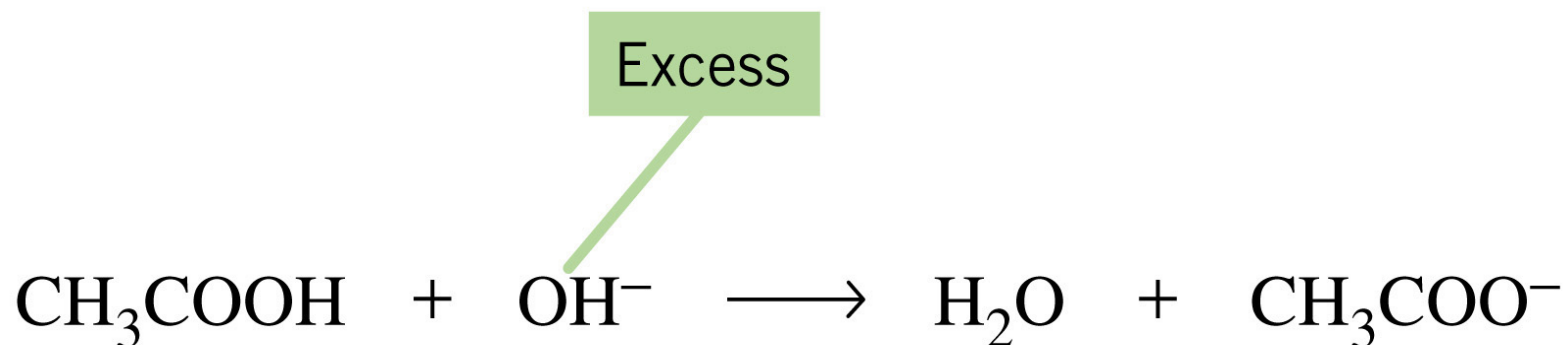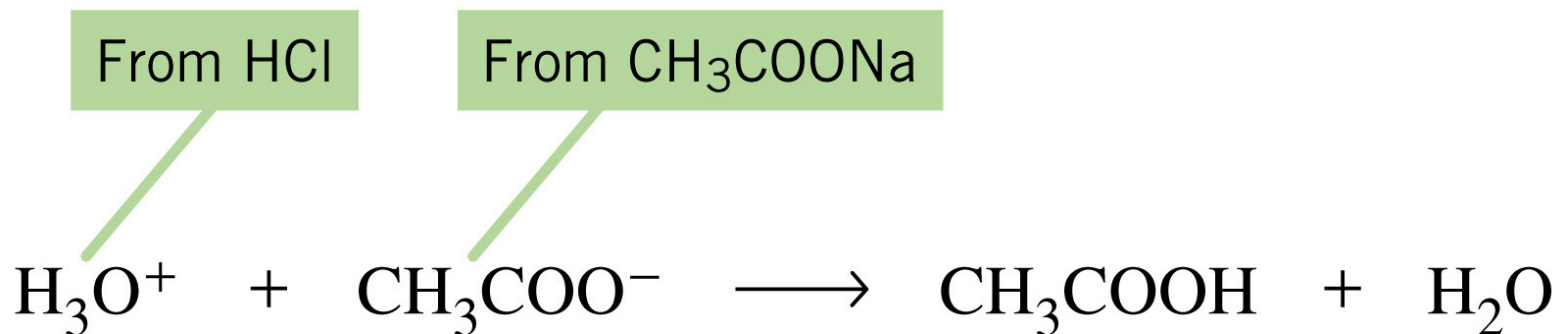*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Buffer Solutions

The acid component of the buffer can neutralize small added amounts of OH$^-$, and the basic component can neutralize small added amounts of H$_3$O$^+$

When a salt supplies CH$_3$COO$^-$, equilibrium shifts to the *left*.

$$CH_3COOH \ + \ H_2O \ \rightleftharpoons \ H_3O^+ \ + \ CH_3COO^-$$

Acid        Base              Acid              Base

EOS

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Buffering Action

From HCl

From $CH_3COONa$

$$H_3O^+ \; + \; CH_3COO^- \longrightarrow CH_3COOH \; + \; H_2O$$

Excess

$$CH_3COOH \; + \; OH^- \longrightarrow H_2O \; + \; CH_3COO^-$$

EOS

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# Buffer Solutions (cont'd)

- The acid component of the buffer neutralizes small added amounts of OH−, forming the *weaker* conjugate base which does not affect pH much:

$$HA + \mathbf{OH^-} \rightarrow H_2O + \mathbf{A^-}$$

- The base component neutralizes small added amounts of $H_3O^+$, forming the *weaker* conjugate acid which does not affect pH much.

$$A^- + \mathbf{H_3O^+} \rightarrow H_2O + \mathbf{HA}$$

- Pure water does not buffer at all …

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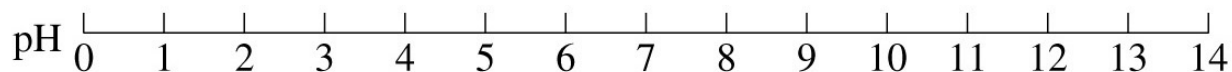
Chapter Fifteen

**Pure water *increases* in pH by about 5 pH units when the OH⁻ is added, and *decreases* by about 5 pH units when the H₃O⁺ is added.**

**Water**

1.00 L water + 0.010 mol OH⁻

1.00 L water

1.00 L water + 0.010 mol H₃O⁺

pH  0  1  2  3  4  5  6  7  8  9  10  11  12  13  14

**Buffer solution**

1.00 L buffer + 0.010 mol OH⁻

1.00 L buffer

1.00 L buffer + 0.010 mol H₃O⁺

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**In contrast, the same amounts of OH⁻ and H₃O⁺ added to a buffer solution barely change the pH.**

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# An Equation for Buffer Solutions

## *Buffer Calculations*

- Since a buffer contains both a weak acid and its conjugate base, we can use the standard equation for the dissociation of an acid to represent the reaction, using the concentration of the weak acid as [HA] and the concentration of the weak base as [A⁻]:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$$
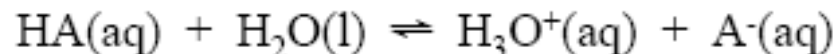
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

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

# An Equation for Buffer Solutions

## *The Henderson-Hasselbalch Equation*

- For any weak acid, the $K_a$ expression is:

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

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

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

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

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# An Equation for Buffer Solutions

- In certain applications, there is a need to repeat the calculations of the pH of buffer solutions many times. This can be done with a single, simple equation, but there are some limitations.

- The *Henderson–Hasselbalch equation*:

$$ pH = pK_a + \log \frac{[base]}{[acid]} $$

- To use this equation, the ratio [conjugate base]/[weak acid] must have a value between 0.10–10 and both concentrations must exceed $K_a$ by a factor of 100 or more.

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# Example 15.17

A buffer solution is 0.24 M $NH_3$ and 0.20 M $NH_4Cl$. **(a)** What is the pH of this buffer? **(b)** If 0.0050 mol NaOH is added to 0.500 L of this solution, what will be the pH?

# Example 15.18

What concentration of acetate ion in 0.500 M $CH_3COOH$(aq) produces a buffer solution with pH = 5.00?

# Buffer Capacity and Buffer Range

- The **buffer capacity** is the amount of acid or base that can be added to a buffer without destroying its effectiveness.

- A buffer is most effective when the concentrations of the acid and its conjugate base are equal; if the concentrations of acid and base are different by more than a factor of 10, the buffer will not be reasonably effective.

- The more concentrated the components of a buffer are, the greater the buffer capacity.

  - A buffer made from 1.0 M acetic acid and 1.0 M sodium acetate has the same pH as a buffer made from 0.10 M solutions of each, but has a much greater ability to resist pH changes.

- The most effective range for a buffer (the **buffer range**) is within $\pm 1$ pH units of the $pK_a$ of the weak acid.

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1. **Choose the conjugate acid-base pair.** It is best to use a conjugate pair in which the $pK_a$ is within 1 unit of the desired pH of the buffer.

    - For a buffer at a pH of 3.90, formic acid, $HCO_2H$ ( $pK_a$ = 3.74), would be a good choice.

    - The conjugate base can be obtained from an appropriate soluble salt, e.g., sodium formate.

2. **Calculate the ratio of buffer components that gives the desired pH (using the H-H equation).**

$$3.90 = 3.74 + \log ([base]/[acid])$$
$$\log ([base]/[acid]) = 0.16$$
$$[base]/[acid] = 1.4$$

    - Thus, for every 1.0 mol of formic acid, 1.4 mol of sodium formate are needed.

3. **Determine the buffer concentration.** For many laboratory applications, concentrations of 0.50 *M* are suitable, but other concentrations can be used.

    - From the concentration of acid solutions in the available solutions, calculate the mass of conjugate base necessary to make the buffer.

    - E.g., if we have 0.40 *M* formic acid, to make 1.0 L of the buffer, 38 g of sodium formate will be needed).

4. **Mix the solution and adjust the pH.** Once the buffer has been prepared by dissolving the conjugate base in the acid solution, it will probably be necessary to adjust it to the exact pH desired by adding small amounts of strong acid or base.

# Examples: Buffers

4. Which of the following acids would be the best choice to combine with its sodium salt to make a solution buffered at pH 4.25? For the best choice, calculate the ratio of the conjugate base to the acid required to attain the desired pH. (Ex. 16.5)

Chlorous acid, $HClO_2$     $pK_a = 1.95$

Nitrous acid, $HNO_2$     $pK_a = 3.34$

Formic acid, $HCHO_2$     $pK_a = 3.74$

Hypochlorous acid, $HClO$     $pK_a = 7.54$

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# The H-H Equation in Biochemistry

- The Henderson-Hasselbalch equation is important in biochemical applications, because it allows us to quickly calculate the percent dissociation of an acid:

$$\log\left(\frac{[\text{base}]}{[\text{acid}]}\right) = \text{pH} - \text{p}K_a$$

$$\frac{[\text{base}]}{[\text{acid}]} = \text{antilog}(\text{pH} - \text{p}K_a)$$

At pH = $\text{p}K_a$ + 2.00 :   $\dfrac{[\text{base}]}{[\text{acid}]} = 1.0 \times 10^2 = \dfrac{100}{1} \Rightarrow 99\%$ dissociation

At pH = $\text{p}K_a$ + 1.00 :   $\dfrac{[\text{base}]}{[\text{acid}]} = 1.0 \times 10^1 = \dfrac{10}{1} \Rightarrow 91\%$ dissociation

At pH = $\text{p}K_a$ + 0.00 :   $\dfrac{[\text{base}]}{[\text{acid}]} = 1.0 \times 10^0 = \dfrac{1}{1} \Rightarrow 50\%$ dissociation

At pH = $\text{p}K_a$ − 1.00 :   $\dfrac{[\text{base}]}{[\text{acid}]} = 1.0 \times 10^{-1} = \dfrac{1}{10} \Rightarrow 9\%$ dissociation

At pH = $\text{p}K_a$ − 2.00 :   $\dfrac{[\text{base}]}{[\text{acid}]} = 1.0 \times 10^{-2} = \dfrac{1}{100} \Rightarrow 1\%$ dissociation

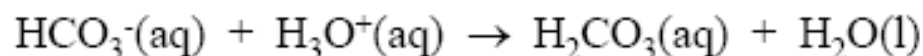*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Why Buffers?

- Human blood is at a pH of 7.4 (often referred to as *physiological pH*). There are a number of buffer systems which maintain this pH, including one involving carbonic acid and the bicarbonate ion:

  - $H_2CO_3$ neutralizes bases in the bloodstream:

  $$H_2CO_3(aq) + OH^-(aq) \rightarrow HCO_3^-(aq) + H_2O(l)$$
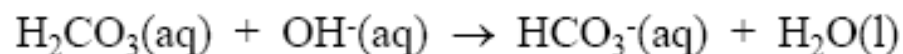
  - Bicarbonate neutralizes acids in the bloodstream:

  $$HCO_3^-(aq) + H_3O^+(aq) \rightarrow H_2CO_3(aq) + H_2O(l)$$

  - Low blood pH results in a condition called *acidosis*, in which the blood's ability to carry oxygen is diminished:

  $$HbH^+(aq) + O_2(g) \rightleftharpoons HbO_2(aq) + H^+(aq)$$

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# Why Buffers?

- Many enzymes work only in a very precise pH range; too much acid or base can denature a protein, causing it to be nonfunctional. Whether they are being used in living cells or in laboratories, buffers are necessary to keep the enzymes at the right pH.

- Buffer solutions formed from citric acid ($H_3C_6H_5O_7$) and sodium citrate ($Na_3C_6H_5O_7$) are used to control pH levels in household cleaners, foods (especially gels and foams, which collapse at the wrong pH), pharmaceuticals, etc.

- Buffers are used in industry to control the pH during fermentation reactions, in dyeing fabrics, and many other processes.

# Acid-Base Titrations

Titration Curves

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Acid–Base Indicators

An acid–base indicator is a weak acid having one color and the conjugate base of the acid having a different color. One of the "colors" may be colorless

Acid–base indicators are often used for applications in which precise pH readings aren't necessary

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# Acid–Base Indicators

- An acid–base *indicator* is a weak acid or base.

- The acid form (HA) of the indicator has one color, the conjugate base ($A^-$) has a different color. One of the "colors" may be colorless.

- In an acidic solution, $[H_3O^+]$ is high. Because $H_3O^+$ is a common ion, it suppresses the ionization of the indicator acid, and we see the color of HA.

- In a basic solution, $[OH^-]$ is high, and it reacts with HA, forming the color of $A^-$.

- Acid–base indicators are often used for applications in which a precise pH reading isn't necessary.

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# Acid–Base Indicators

A common indicator used in introductory chemistry laboratories is litmus



Blue in base

Red in acid
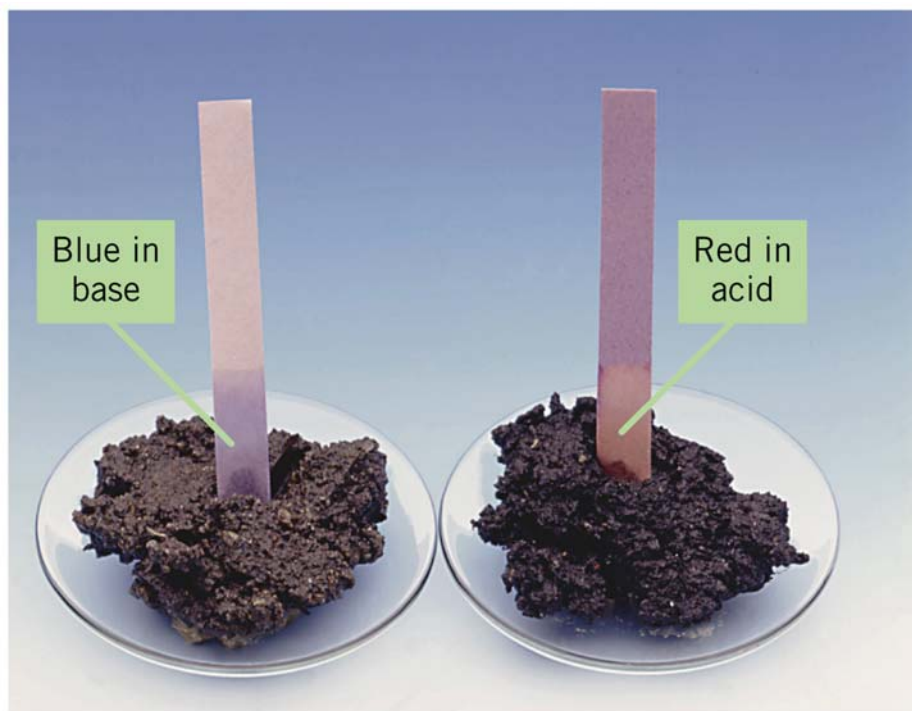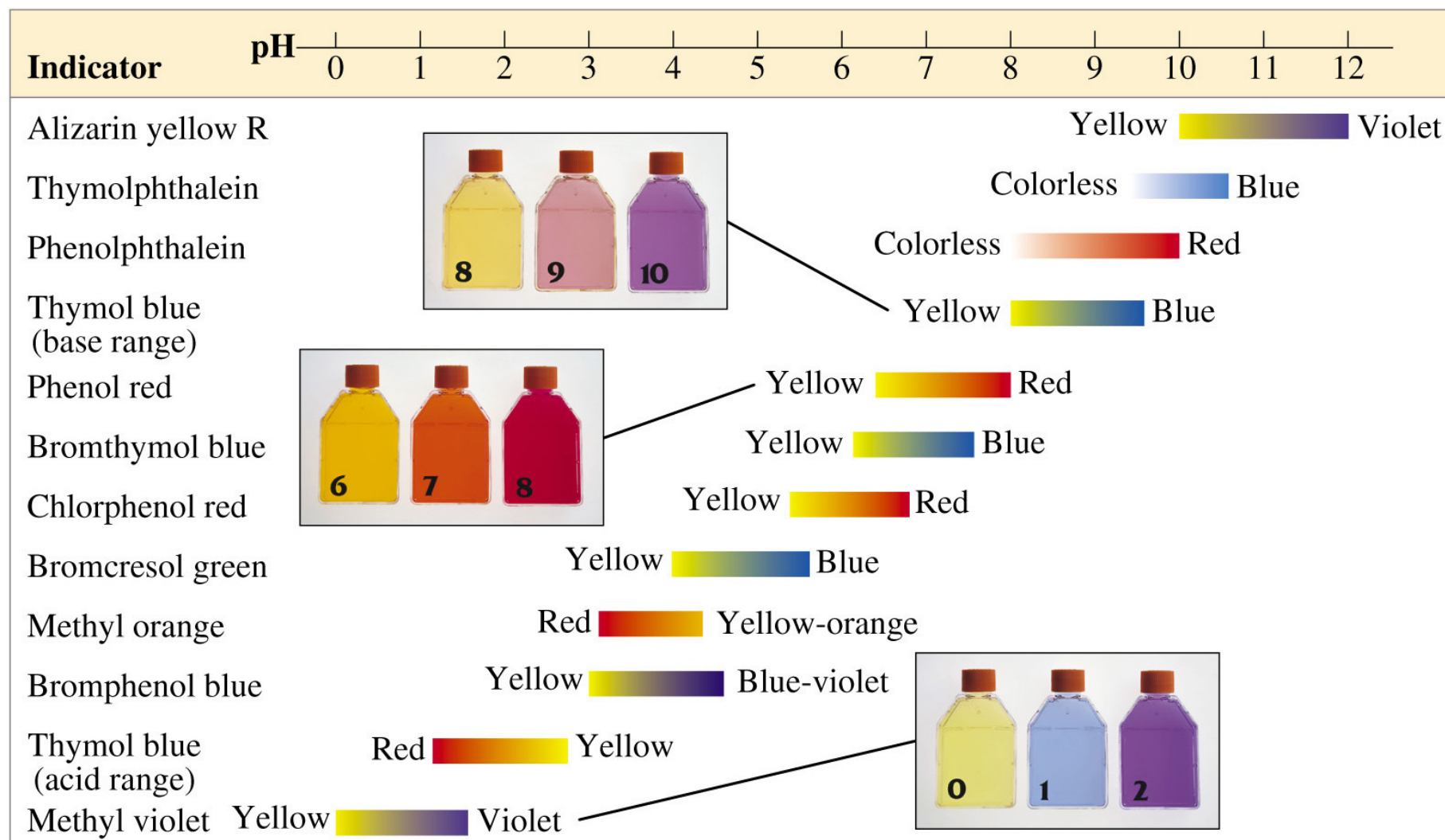
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In an acidic solution, $[H_3O^+]$ is high. Because $H_3O^+$ is a common ion, it suppresses the ionization of the indicator acid

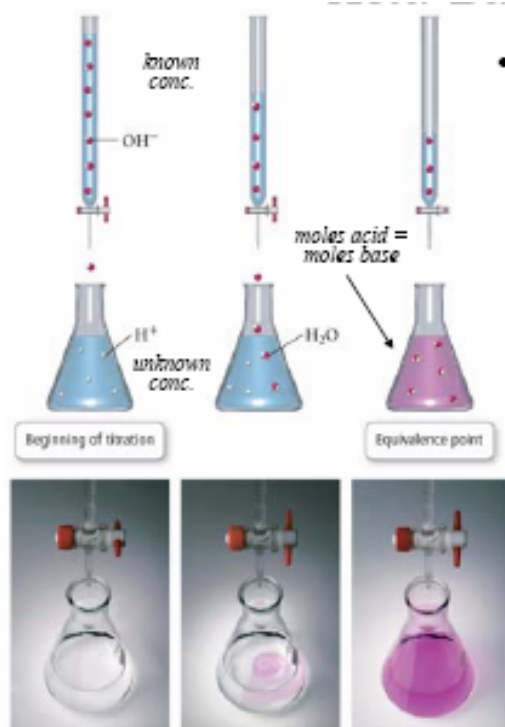*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Different indicators have different values of $K_a$, so they exhibit color changes at different values of pH …



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# Acid-Base Titrations



- In an **acid-base titration**, a solution acid or base with an unknown concentration (in the Erlenmeyer flask) is reacted with a solution of base or acid of known concentration (in the buret), until the number of moles of titrant added equals the number of moles in the solution being titrated. This is the **equivalence point** of the titration (indicated by a color change in an acid-base indicator, or by an electronic pH meter).

# Neutralization Reactions

- At the *equivalence point* in an acid–base titration, the acid and base have been brought together in precise stoichiometric proportions.   *mol acid = mol base*

- The *endpoint* is the point in the titration at which the indicator changes color.

- Ideally, the indicator is selected so that the endpoint and the equivalence point are very close together.

- The endpoint and the equivalence point for a neutralization titration can be best matched by plotting a *titration curve*, a graph of pH versus volume of titrant.

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

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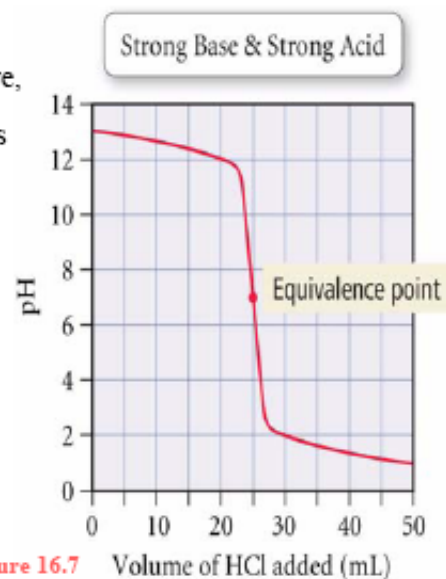# Titration Curve, Strong Acid with Strong Base
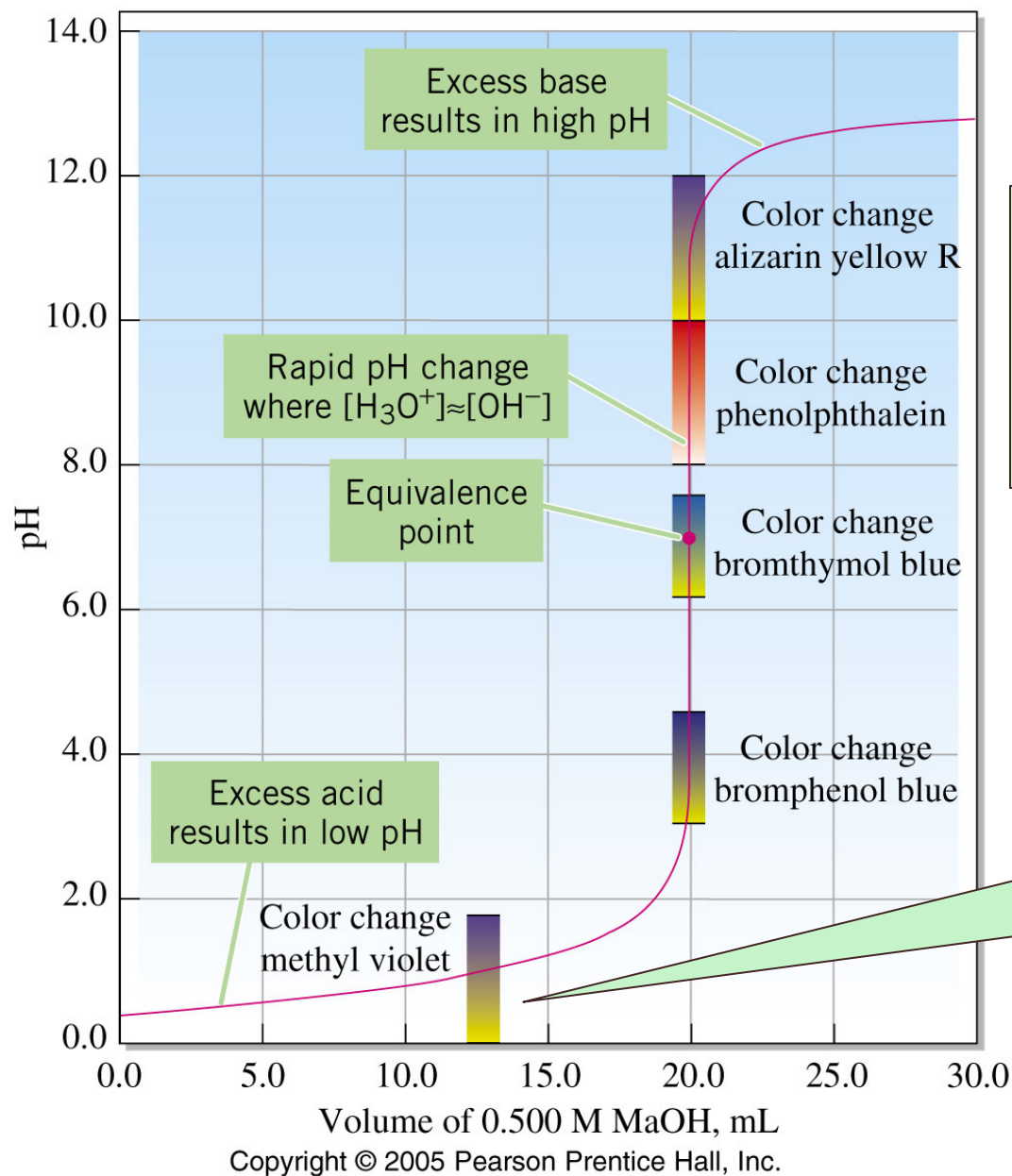


**Bromphenol blue, bromthymol blue, and phenolphthalein all change color at very nearly 20.0 mL**

**At about what volume would we see a color change if we used methyl violet as the indicator?**

Excess base results in high pH

Color change alizarin yellow R

Rapid pH change where $[H_3O^+] \approx [OH^-]$

Color change phenolphthalein

Equivalence point

Color change bromthymol blue

Color change bromphenol blue

Excess acid results in low pH

Color change methyl violet

pH

Volume of 0.500 M MaOH, mL

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Chapter Fifteen

# Strong Base-Strong Acid

- In this titration curve, a strong base (NaOH) is titrated with a strong acid (HCl).

Calculating the pH along this curve is similar to a strong acid-strong base curve, except that the solution starts out basic, and becomes more acidic as the titrant is added.
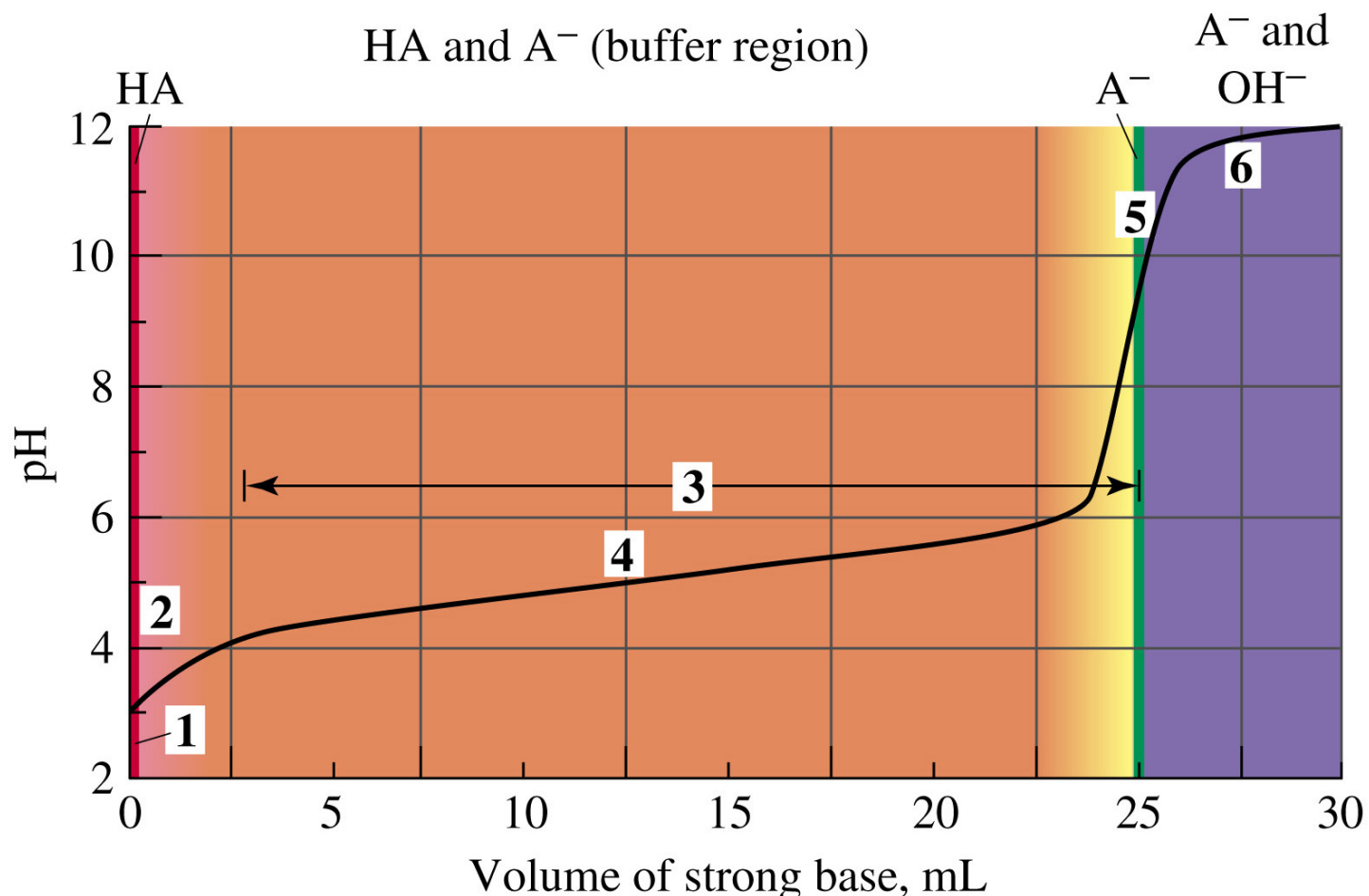
Strong Base & Strong Acid



**Figure 16.7**   Volume of HCl added (mL)

# Titration Curve, Weak Acid with Strong Base
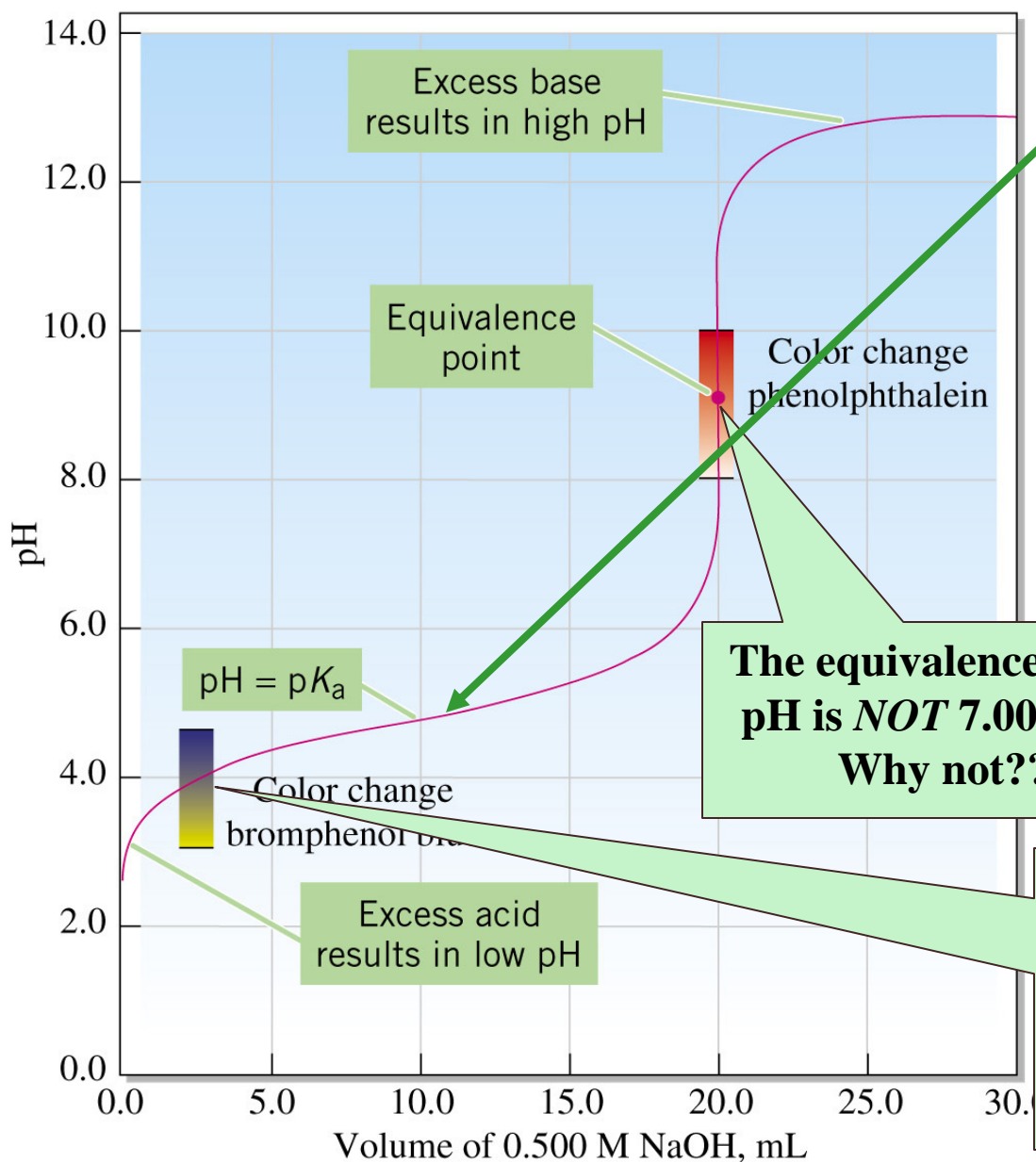


**Buffering** occurs in this system … therefore the Henderson–Hasselbalch equation applies in this region

Excess base results in high pH

Equivalence point

Color change phenolphthalein

pH = p$K_a$

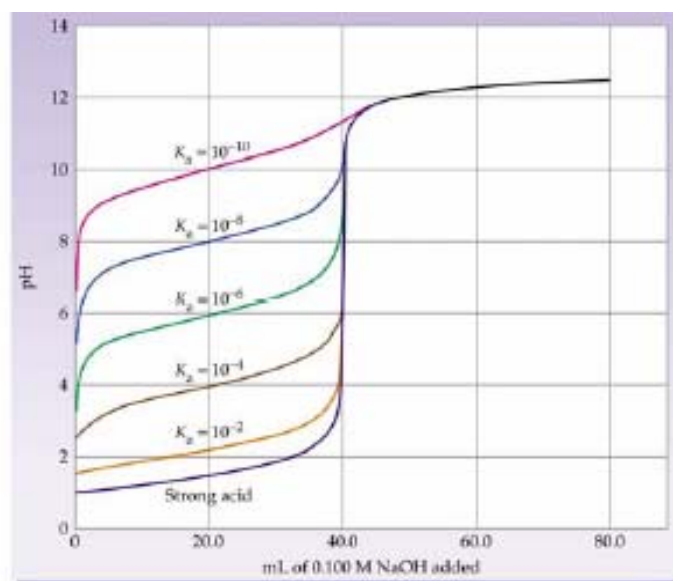Color change bromphenol blue

Excess acid results in low pH

The equivalence-point pH is *NOT* 7.00 here. Why not??

Bromphenol blue was ok for the strong acid/strong base titration, but it changes color far too early to be useful here.

Volume of 0.500 M NaOH, mL

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# Titration Curve for Weak Acid–Strong Base

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# Titration Curves for Various WA-SB Titrations



Titration curves for 40.0 mL of 0.100 M weak acids with 0.100 M NaOH; in all cases, the equivalence point occurs after 40.0 mL of the base is added, but the pH of the equivalence point is higher and more difficult to see for weaker acids.

*General Chemistry* 4th edition, Hill, Petrucci, McCreary, Perry

# Example 15.22    A Conceptual Example

This titration curve shown in Figure 15.18 involves 1.0 M
solutions of an acid and a base. Identify the type of
titration it represents.
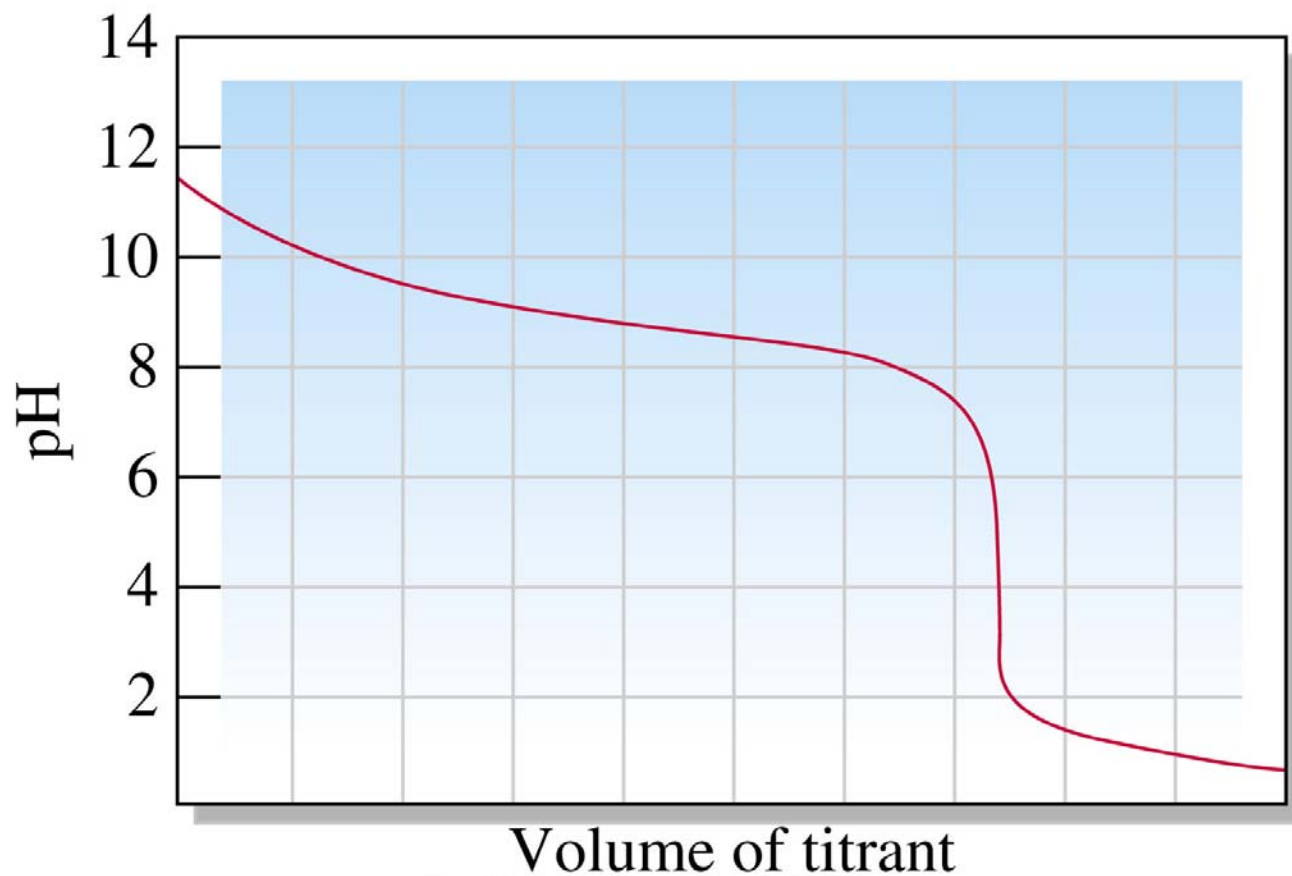


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# Lewis Acids and Bases

- There are reactions in nonaqueous solvents, in the gaseous state, and even in the solid state that can be considered acid–base reactions which Brønsted–Lowry theory is not adequate to explain.

- A *Lewis acid* is a species that is an electron-pair acceptor and a *Lewis base* is a species that is an electron-pair donor.

$$CaO(s) \ + \ SO_2(g) \ \rightarrow \ CaSO_3(s)$$
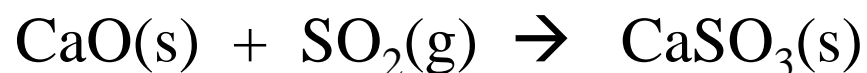
Sulfur accepts an electron pair from the oxygen of CaO

- In organic chemistry, Lewis acids are often called *electrophiles* ("electron-loving") and Lewis bases are often called *nucleophiles* ("nucleus-loving").

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# Lewis Acids and Bases

There are reactions in nonaqueous solvents, in the gaseous state, and even in the solid state that can be considered acid–base reactions in which Brønsted–Lowry theory is not adequate to explain.
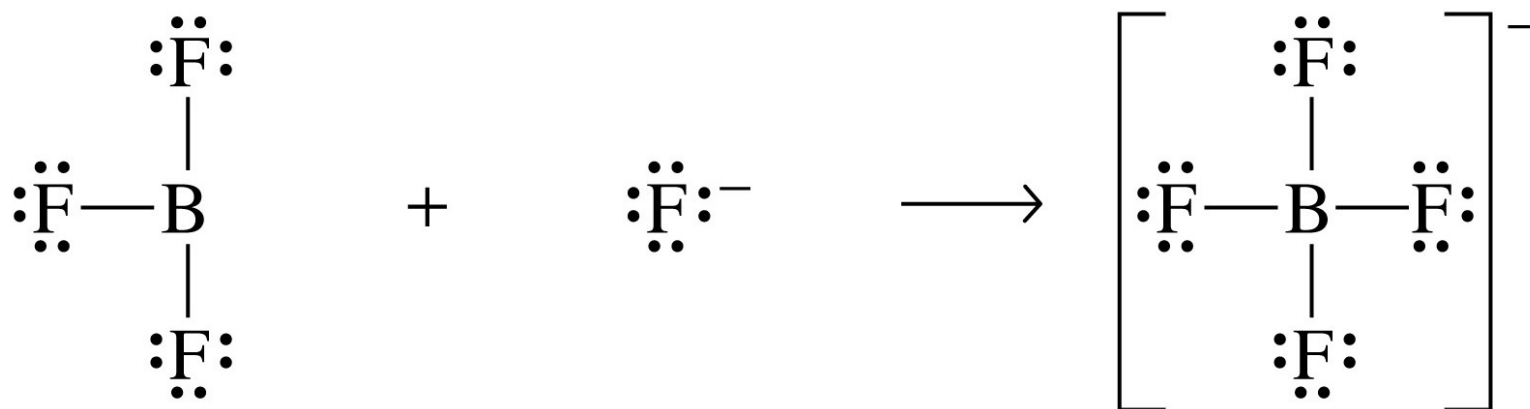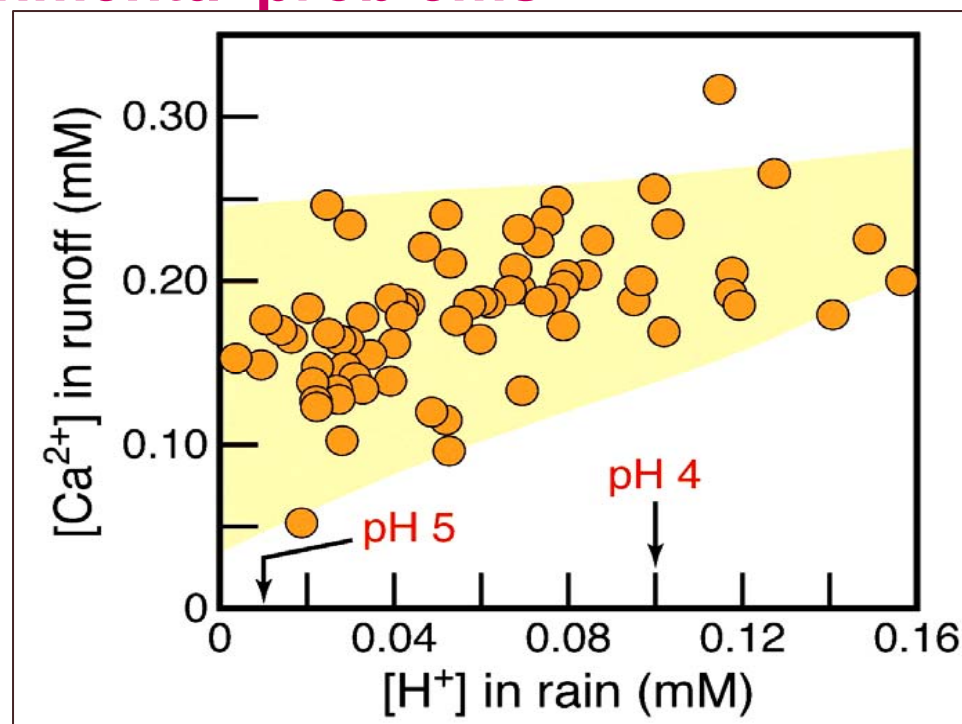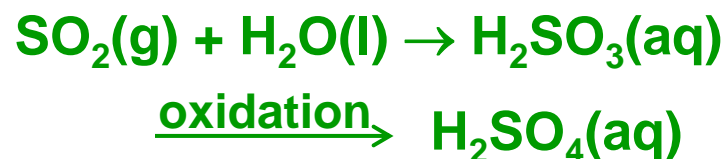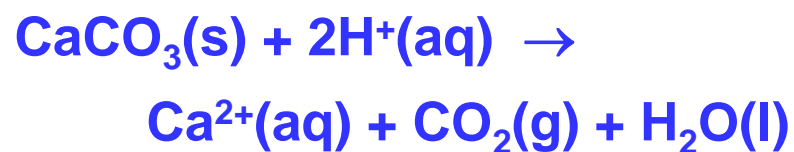


Lewis acid
Electron pair acceptor

Lewis base
Electron pair donor

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# Applications of coupled acid-base equilibria in the modeling of environmental problems

**Found [Ca] in acid rain that has washed off marble stone (largely $CaCO_3$) increases as the $[H^+]$ of acid rain increases.**

$CaCO_3(s) + 2H^+(aq) \rightarrow$

$\qquad Ca^{2+}(aq) + CO_2(g) + H_2O(l)$

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$

$\qquad \underset{\text{oxidation}}{\longrightarrow} H_2SO_4(aq)$

**Al is usually "locked" into insoluble minerals e.g. kaolinite and bauxite. But due to acid rain, soluble forms of Al are introduced into the environment. (Similarly with other minerals containing Hg, Pb etc.)**

**Total [Al] as a function of pH in 1000 Norwegian lakes.**

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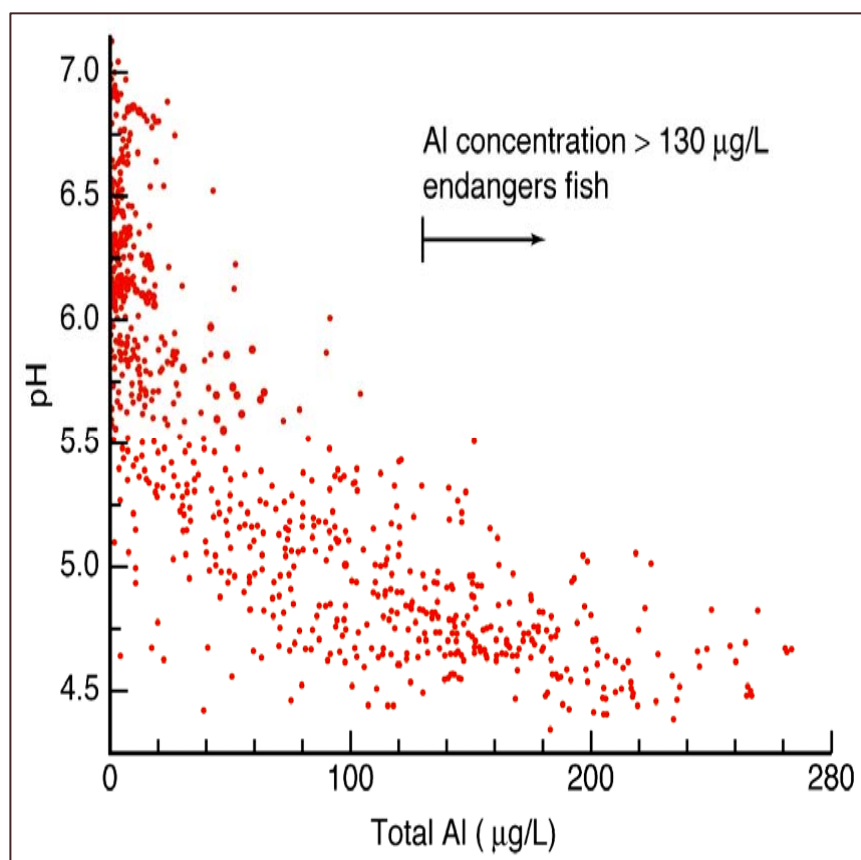
# Summary of Concepts

- In the Brønsted–Lowry theory an acid is a proton donor and a base is a proton acceptor

- If an acid is strong, its conjugate base is weak; and if a base is strong, its conjugate acid is weak

- Water is amphiprotic: it can be either an acid or a base. It undergoes limited self-ionization producing $H_3O^+$ and $OH^-$

- The pH in both pure water and in neutral solutions is 7. Acidic solutions have a pH less than 7 and basic solutions have a pH greater than 7

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# Summary (cont'd)

- In aqueous solutions at 25 ºC, pH + pOH = 14.00
- pH = −log[$H_3O^+$] pOH = −log[$OH^-$] p$K_w$ = −log$K_w$
- Hydrolysis reactions cause certain salt solutions to be either acidic or basic
- A strong electrolyte that produces an ion common to the ionization equilibrium of a weak acid or a weak base suppresses the ionization of the weak electrolyte
- Acid–base indicators are weak acids for which the acid and its conjugate base have different colors

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# Summary (cont'd)

- In Lewis acid–base theory, a Lewis acid accepts an electron pair and a Lewis base donates an electron pair

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Chapter Fifteen