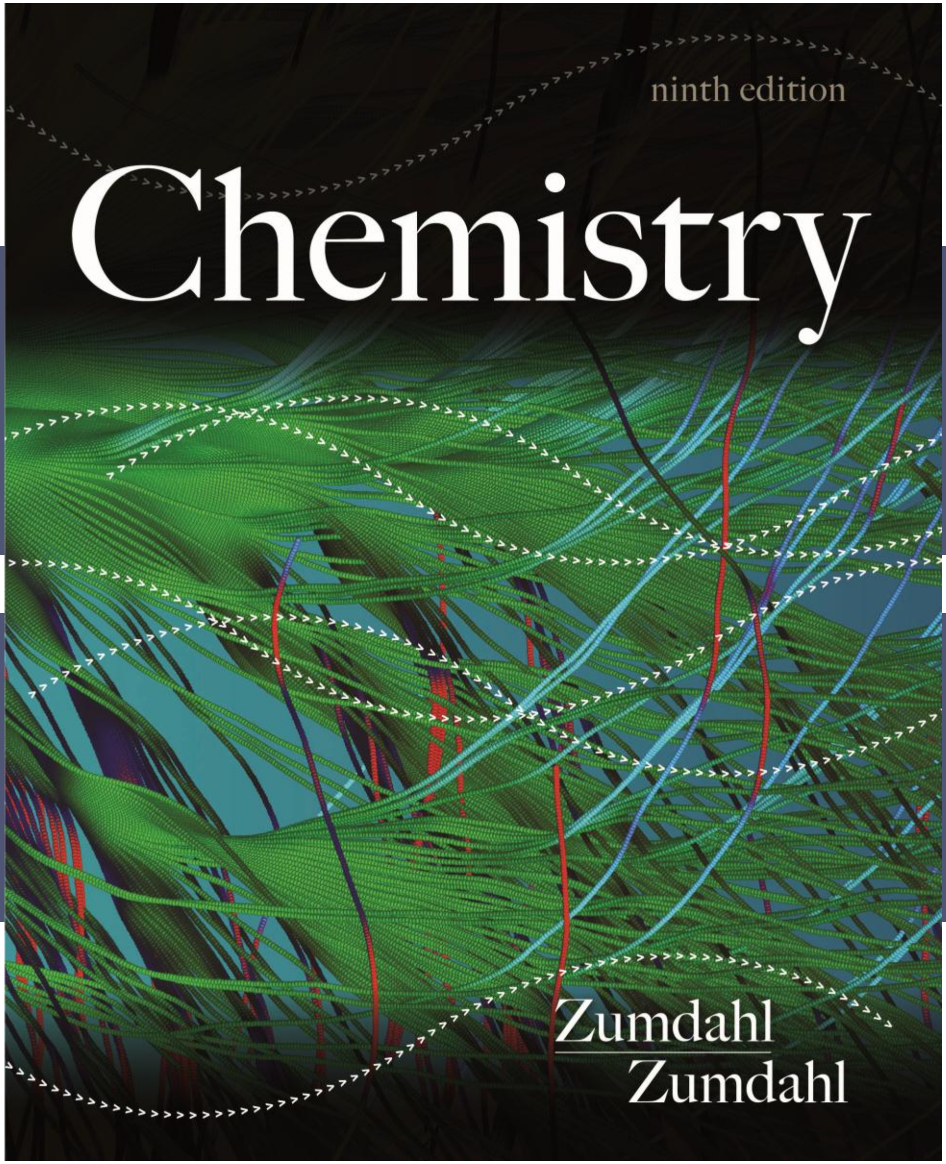

Chapter 14

Acids and Bases

Chapter 14

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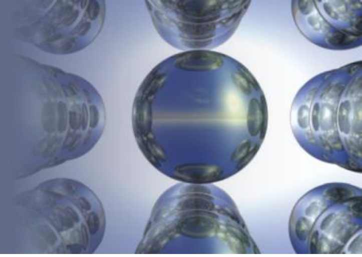

Chapter 14
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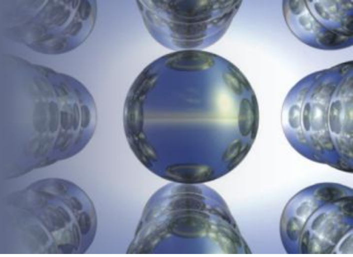
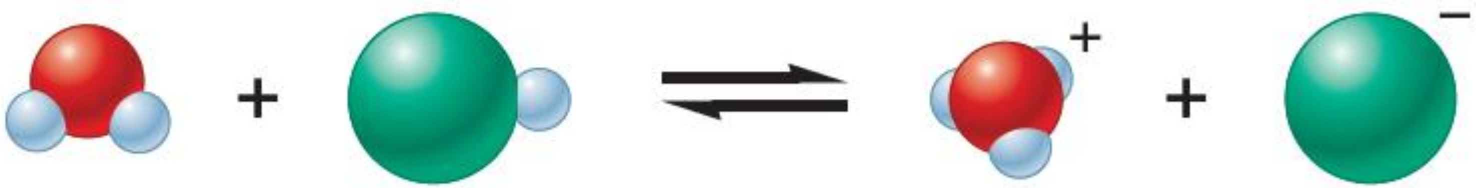


Nature of Acids and Bases

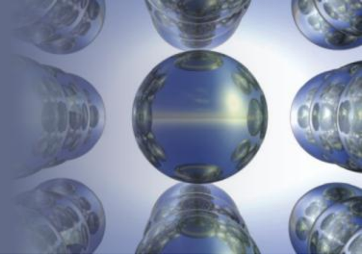
- **Arrhenius concept**: Acids produce hydrogen ions in aqueous solution, and bases produce hydroxide ions
  - Limited application
- **Brønsted–Lowry model**: Acids are proton (H^+) donors, and bases are proton acceptors

Acid in Water

- Gaseous HCl dissolves in water by the following reaction:



  - The proton is transferred from the HCl molecule to the water molecule
    - Leads to the formation of **hydronium ion**, H_3O^+



Acid in Water - General Reaction

- Reaction

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Acid
Base
Conjugate acid
Conjugate base

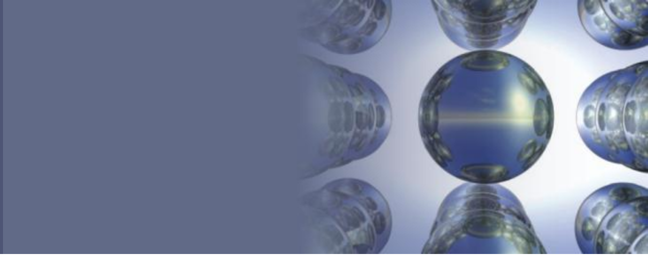
  - **Conjugate base**: Remains of an acid molecule after it loses a proton
  - **Conjugate acid**: Formed when a proton is transferred to a base
  - **Conjugate acid–base pair**: Two substances related to each other by accepting and donating a single proton

Acid in Water - General Reaction (Continued)

- Equilibrium expression

$$K_\mathrm{a} = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

  - K_a is the **acid dissociation constant**
- Water can be omitted from the acid dissociation reaction
  - Does not affect the equilibrium position



Interactive Example 14.1 - Acid Dissociation (Ionization) Reactions

- Write the simple dissociation (ionization) reaction (omitting water) for each of the following acids:
  a. Hydrochloric acid (HCl)
  b. Acetic acid ($HC_2H_3O_2$)
  c. The anilinium ion ($C_6H_5NH_3^+$)
  d. The hydrated aluminum(III) ion $[Al(H_2O)_6]^{3+}$

Interactive Example 14.1 - Solution

a. $\mathrm{HCl}(aq) \rightleftharpoons \mathrm{H}^{+}(aq) + \mathrm{Cl}^{-}(aq)$

b. $\mathrm{HC_2H_3O_2}(aq) \rightleftharpoons \mathrm{H}^{+}(aq) + \mathrm{C_2H_3O_2^{-}}(aq)$

c. $\mathrm{C_6H_5NH_3^{+}}(aq) \rightleftharpoons \mathrm{H}^{+}(aq) + \mathrm{C_6H_5NH_2}(aq)$

Interactive Example 14.1 - Solution (Continued)

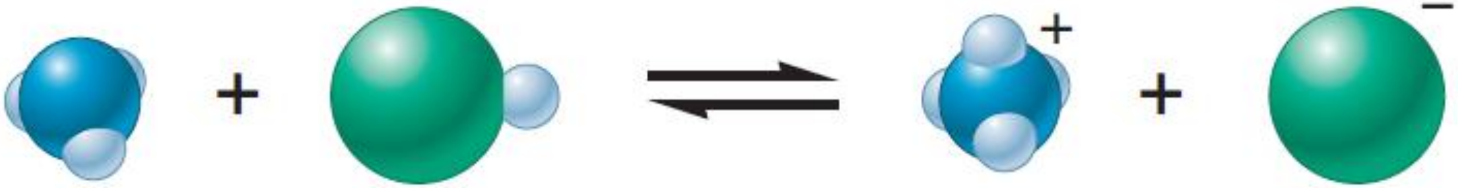
d. Although this formula looks complicated, writing the reaction is simple if you concentrate on the meaning of K_a
   - Removing a proton, which can come only from one of the water molecules, leaves one OH^- and five H_2O molecules attached to the Al^{3+} ion
     - So the reaction is

$$\mathrm{Al(H_2O)_6^{3+}}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{Al(H_2O)_5OH^{2+}}(aq)$$

Brønsted–Lowry Model

- Can be extended to reactions in the gas phase
- When HCl and NH_3 diffuse, HCl donates a proton to NH_3

$$NH_3(g) + HCl(g) \rightleftharpoons NH_4Cl(s)$$



Strength of an Acid

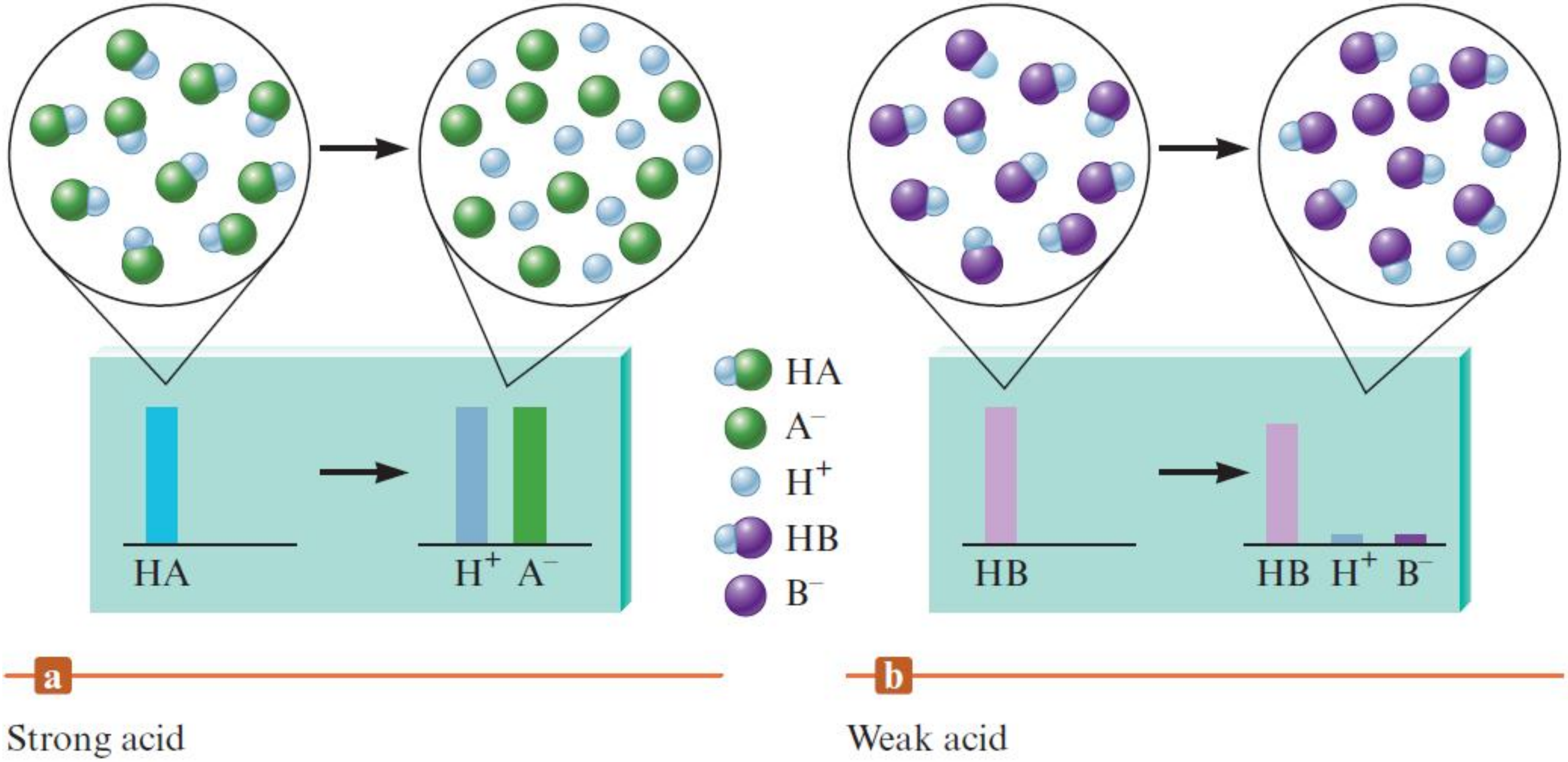
- Defined by the equilibrium position of the acid’s ionization reaction

$$\mathrm{HA}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{A^-}(aq)$$

Acid Conjugate base

  - **Strong acid**: Equilibrium lies far to the right
    - Yields a weak conjugate base
  - **Weak acid**: Equilibrium lies far to the left
    - Weaker the acid, stronger its conjugate base

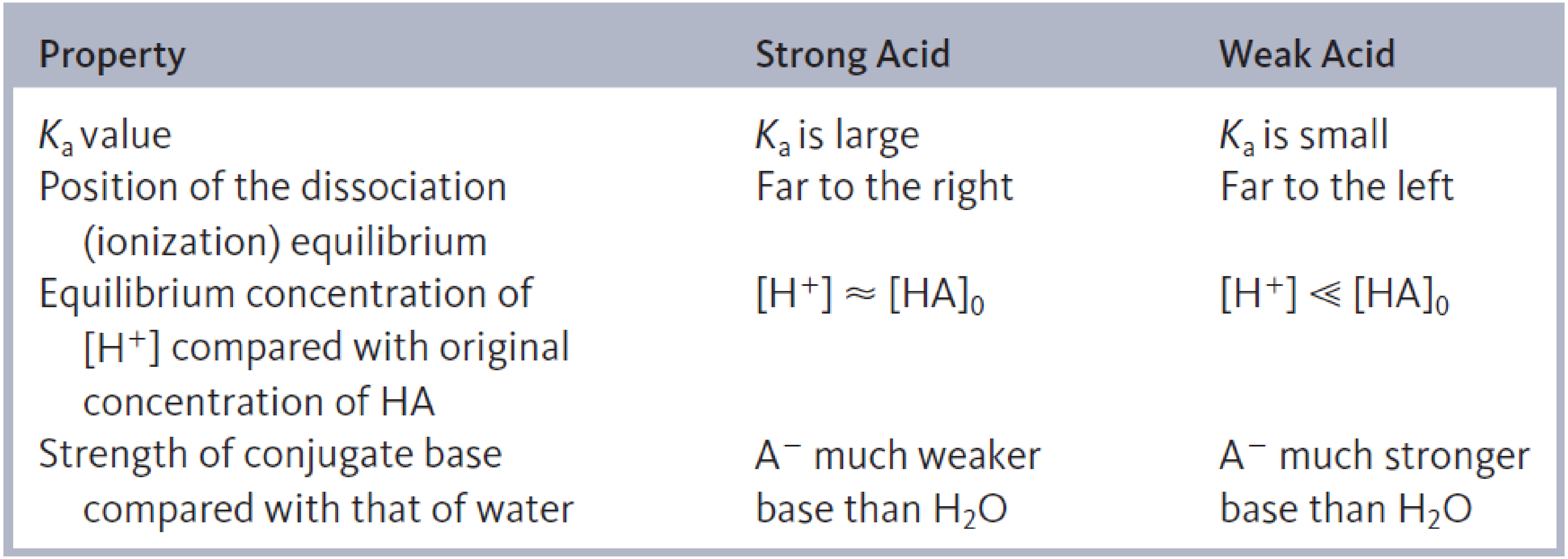
Figure 14.4 - Strong and Weak Acids



Strong acid

Weak acid

Table 14.1 - Various Ways to Describe Acid Strength



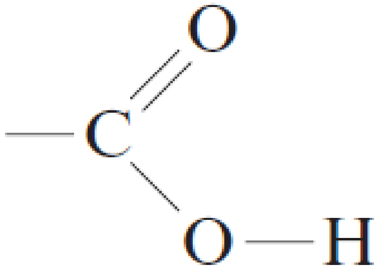
Property	Strong Acid	Weak Acid
K_a value	K_a is large	K_a is small
Position of the dissociation (ionization) equilibrium	Far to the right	Far to the left
Equilibrium concentration of $[H^+]$ compared with original concentration of HA	$[H^+] \approx [HA]_0$	$[H^+] \ll [HA]_0$
Strength of conjugate base compared with that of water	A^- much weaker base than H_2O	A^- much stronger base than H_2O

Types of Acids

- **Diprotic acids**: Composed of two acidic protons
    - Completely dissociate in water
    - Example - Sulfuric acid [H_2SO_4 (*aq*)]
- **Oxyacids**: Acidic proton is attached to an oxygen atom
    - Examples - Nitric acid [HNO_3(aq)] and phosphoric acid (H_3PO_4)

Types of Acids (Continued 1)

- **Organic acids**: Contain a carbon atom backbone
  - Contain the **carboxyl group**



  - Generally weak in nature
  - Examples - Acetic acid (CH_3COOH) and benzoic acid (C_6H_5COOH)

Types of Acids (Continued 2)

- Hydrohalic acids (HX)
  - Acidic proton is attached to an atom other than oxygen
  - X - Halogen atom
- **Monoprotic acids**: Contain one acidic proton
  - Examples - Hydrogen sulfate ion (HSO_4^-) and phenol (HOC_6H_5)

Critical Thinking

- Vinegar contains acetic acid and is used in salad dressings
  - What if acetic acid was a strong acid instead of a weak acid?
    - Would it be safe to use vinegar as a salad dressing?

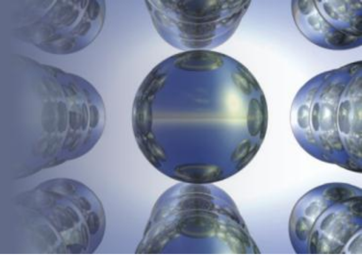
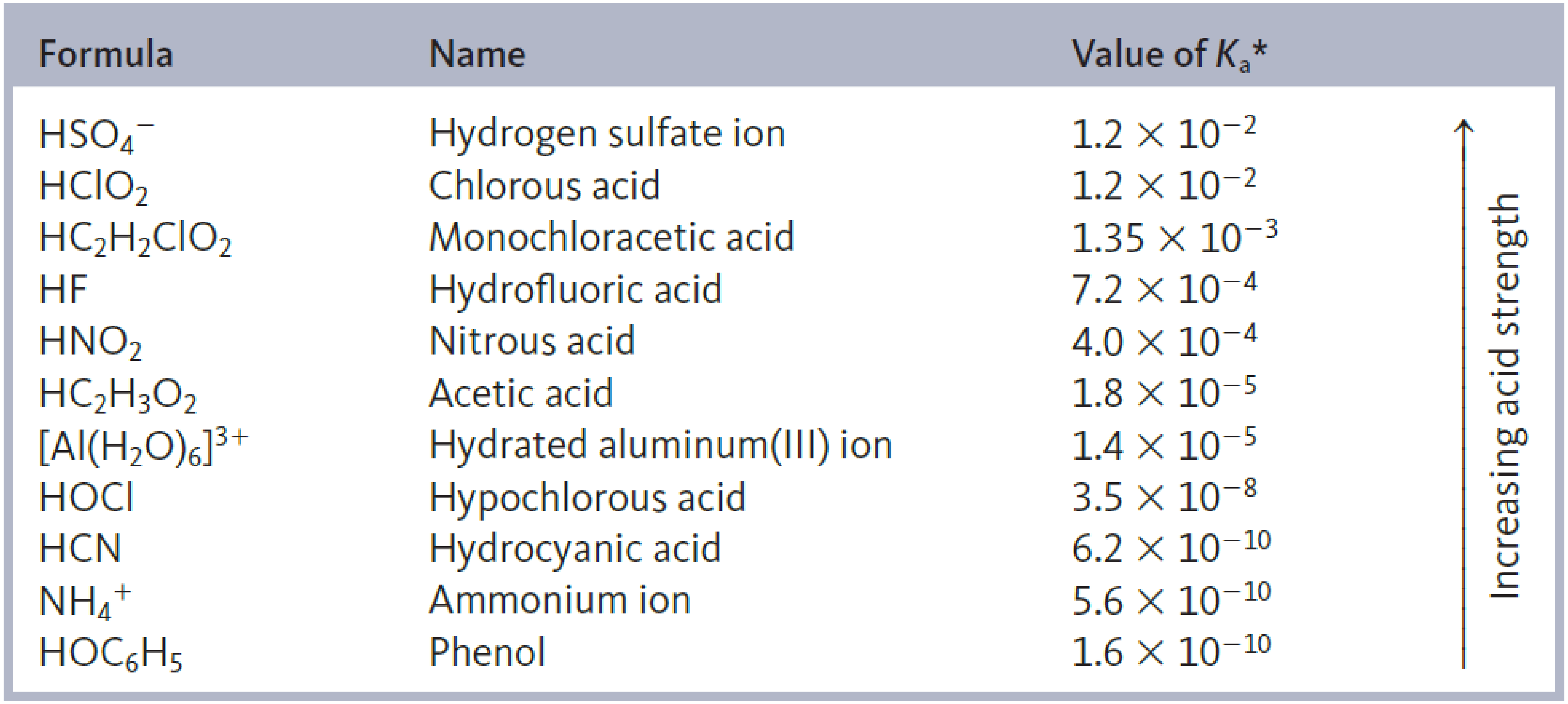


Table 14.2 - Values of K_a for Some Common Monoprotic Acids



Formula	Name	Value of K_a*
HSO_4^-	Hydrogen sulfate ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$HC_2H_2ClO_2$	Monochloracetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
$HC_2H_3O_2$	Acetic acid	1.8×10^{-5}
$[Al(H_2O)_6]^{3+}$	Hydrated aluminum(III) ion	1.4×10^{-5}
$HOCl$	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

*The units of K_a are customarily omitted.

Interactive Example 14.2 - Relative Base Strength

- Using Table 14.2, arrange the following species according to their strengths as bases:
  - H_2O, F^-, Cl^-, NO_2^-, and CN^-

Interactive Example 14.2 - Solution

- Remember that water is a stronger base than the conjugate base of a strong acid but a weaker base than the conjugate base of a weak acid, which leads to the following order:

$$Cl^- < H_2O < \text{conjugate bases of weak acids}$$

Weakest bases ⟶ Strongest bases

Interactive Example 14.2 - Solution (Continued 1)

- We can order the remaining conjugate bases by recognizing that the strength of an acid is inversely related to the strength of its conjugate base
  - From the table, we have

$$K_a \text{ for HF} > K_a \text{ for HNO}_2 > K_a \text{ for HCN}$$

Interactive Example 14.2 - Solution (Continued 2)

- The base strengths increase as follows:

$$F^- < NO_2^- < CN^-$$

- The combined order of increasing base strength is

$$Cl^- < H_2O < F^- < NO_2^- < CN^-$$

Water as an Acid and a Base

- Water is an **amphoteric substance**
  - **Amphoteric**: Substance that behaves either as an acid or as a base
  - Depicted in the autoionization of water
    - **Autoionization**: Transfer of a proton from one water molecule to another to produce a hydroxide ion and a hydronium ion
    - One water molecule acts as an acid by furnishing a proton, and the other acts as a base by accepting the proton

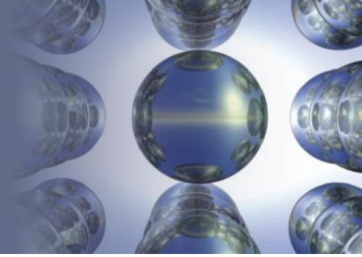
Autoionization Reaction for Water

$$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

- Equilibrium expression

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

  - **Ion-product constant (*K*$_w$)** (or the **dissociation constant** for water) always refers to the autoionization of water

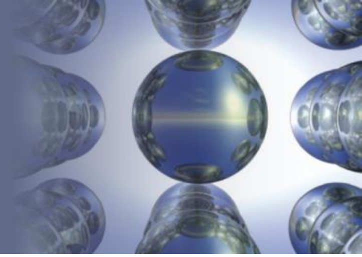


Ion-Product Constant (K_w)

- No matter what the solution contains, the product of $[H^+]$ and $[OH^-]$ must always equal 1.0×10^{-14} at 25° C

$$K_\text{w} = \left[\text{H}^+\right]\left[\text{OH}^-\right] = \left(1.0\times10^{-7}\right)\left(1.0\times10^{-7}\right)$$
$$= 1.0\times10^{-14}$$

- Temperature dependent



Possible Situations of K_w

- $[H^+] = [OH^-]$
  - Neutral solution
- $[H^+] > [OH^-]$
  - Acidic solution
- $[OH^-] > [H^+]$
  - Basic solution

Example 14.4 - Autoionization of Water

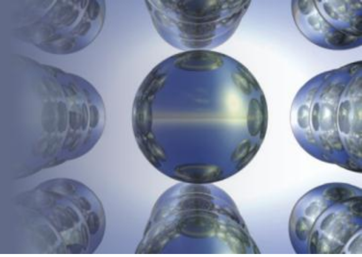
- At 60° C, the value of K_w is 1×10^{-13}
  a. Using Le Châtelier’s principle, predict whether the following reaction is exothermic or endothermic:

$$2\text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OH}^-(aq)$$

  b. Calculate [H^+] and [OH^-] in a neutral solution at 60° C

Example 14.4 - Solution (a)

- K_w increases from 1×10^{-14} at 25° C to 1×10^{-13} at 60° C
    - Le Châtelier's principle states that if a system at equilibrium is heated, it will adjust to consume energy
        - Since the value of K_w increases with temperature, we must think of energy as a reactant, and so the process must be endothermic



Example 14.4 - Solution (b)

- At 60° C,

$$\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=1\times10^{-13}$$

- For a neutral solution,

$$\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]=\sqrt{1\times10^{-13}}=3\times10^{-7}\,M$$

pH Scale

- Helps represent solution acidity
- Log scale based on 10, where

$$\text{pH} = -\log[\text{H}^+]$$

  - pH decreases as $[\text{H}^+]$ increases
  - For a solution where $[\text{H}^+] = 1.0 \times 10^{-7}\ M$
    - $\text{pH} = -\,(-7.00) = 7.00$

Significant Figures

- Number of decimal places in the log is equal to the number of significant figures in the original number

2 significant figures

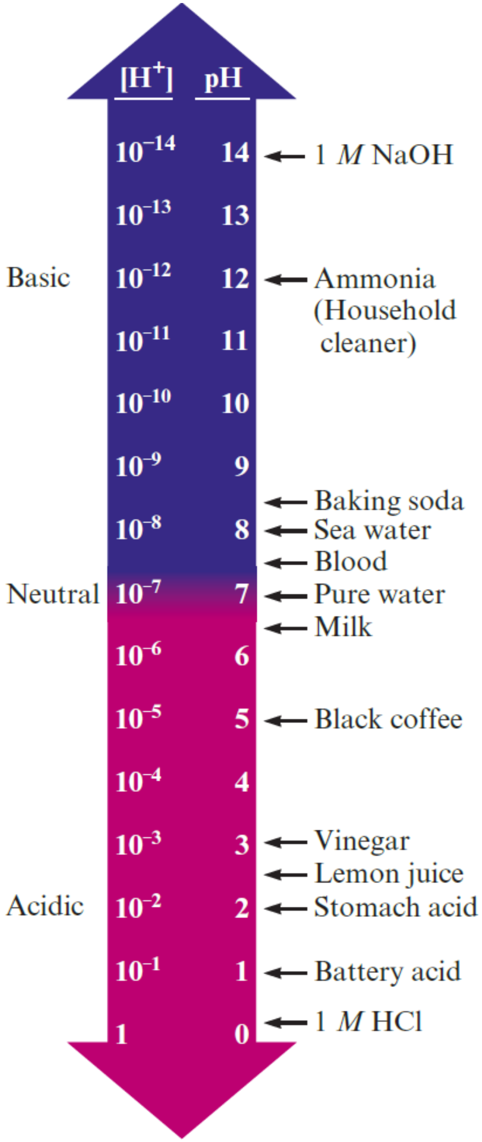
$$[H^+] = 1.0 \times 10^{-9}\ M$$

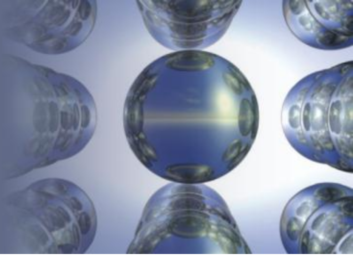
$$\mathrm{pH} = 9.00$$

2 decimal places

Log Scales

- pOH = $-\log [OH^-]$
- pK = $-\log K$
- pH is a log scale based on 10
  - pH changes by 1 for every power of 10 change in $[H^+]$





pH Meter

- Electronic device with a probe that can be inserted into a solution of an unknown pH
  - Probe contains an acidic aqueous solution enclosed by a special glass membrane that permits migration of H^+ ions
- Electric potential results if the unknown solution has a different pH from the solution in the probe

Figure 14.7 - pH Meter

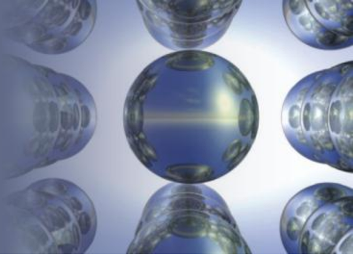
Charles D. Winters

Critical Thinking

- What if you lived on a planet identical to the earth but for which room temperature was 50° C?
    - How would the pH scale be different?

Interactive Example 14.5 - Calculating pH and pOH

- Calculate pH and pOH for each of the following solutions at 25° C
  a. 1.0×10^{-3} *M* OH^{-}
  b. 1.0 *M* OH^{-}



Interactive Example 14.5 - Solution (a)

$$\left[\mathrm{H}^+\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH}^-\right]} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-3}} = 1.0 \times 10^{-11}\,M$$

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right] = -\log\left(1.0 \times 10^{-11}\right) = 11.00$$

$$\mathrm{pOH} = -\log\left[\mathrm{OH}^-\right] = -\log\left(1.0 \times 10^{-3}\right) = 3.00$$

Interactive Example 14.5 - Solution (b)

$$\left[\mathrm{OH}^-\right] = \frac{K_\mathrm{w}}{\left[\mathrm{H}^+\right]} = \frac{1.0 \times 10^{-14}}{1.0} = 1.0 \times 10^{-14}\,M$$

$$\mathrm{pH} = -\log\left[\mathrm{H}^+\right] = -\log(1.0) = 0.00$$

$$\mathrm{pOH} = -\log\left[\mathrm{OH}^-\right] = -\log\left(1.0 \times 10^{-14}\right) = 14.00$$

pH and pOH

- Consider the log of the expression $K_w = [H^+][OH^-]$

$$\log K_w = \log[H^+] + \log[OH^-]$$

or

$$-\log K_w = -\log[H^+] - \log[OH^-]$$

$$pK_w = pH + pOH$$

Since $K_w = 1.0 \times 10^{-14}$, $pK_w = -\log(1.0 \times 10^{-14}) = 14.00$

- Thus, for any solution at 25° C, $pH + pOH = 14.00$

Interactive Example 14.6 - Calculations Using pH

- The pH of a sample of human blood was measured to be 7.41 at 25° C
  - Calculate pOH, $[H^+]$, and $[OH^-]$ for the sample

Interactive Example 14.6 - Solution

- Since pH + pOH = 14.00,

$$\text{pOH} = 14.00 - \text{pH} = 14.00 - 7.41 = 6.59$$

- To find $[H^+]$ we must go back to the definition of pH, which is $\text{pH} = -\log[H^+]$
  - Thus, $7.41 = -\log[H^+]$ or $\log[H^+] = -7.41$

Interactive Example 14.6 - Solution (Continued 1)

- We need to know the antilog of –7.41
    - Taking the antilog is the same as exponentiation

$$\text{antilog}\ (n) = 10^{n}$$

    - Since $\text{pH} = -\log[\text{H}^+]$,

$$-\text{pH} = \log[\text{H}^+]$$

    - $[\text{H}^+]$ can be calculated by taking the antilog of –pH

$$[\text{H}^+] = \text{antilog}\ (-\text{pH})$$

Interactive Example 14.6 - Solution (Continued 2)

- In the present case,

$$[\mathrm{H}^+] = \text{antilog}\ (-\mathrm{pH}) = \text{antilog}\ (-7.41) = 10^{-7.41}$$

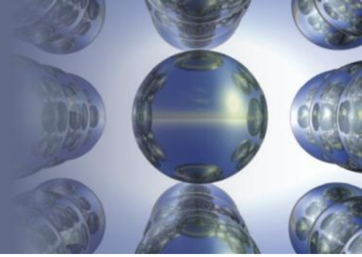
$$[\mathrm{H}^+] = 3.9 \times 10^{-8}\ M$$

- Similarly,

$$[\mathrm{OH}^-] = \text{antilog}\ (-\mathrm{pOH}),$$

- And

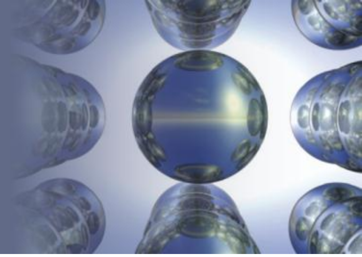
$$[\mathrm{OH}^-] = \text{antilog}\ (-6.59) = 10^{-6.59} = 2.6 \times 10^{-7}\ M$$



Exercise

- Fill in the missing information in the following table:

	pH	pOH	$[H^+]$	$[OH^-]$	Acidic, Basic, or Neutral?
Solution a	6.88	**7.12**	**1.3×10^{-7} *M***	**7.6×10^{-8} *M***	**acidic**
Solution b	**0.92**	**13.08**	**0.12 *M***	8.4×10^{-14} *M*	**acidic**
Solution c	**10.89**	3.11	**1.3×10^{-11} *M***	**7.8×10^{-4} *M***	**basic**
Solution d	**7.00**	**7.00**	1.0×10^{-7} *M*	**1.0×10^{-7} *M***	**neutral**



Solving for pH

- Focus on the solution components and their chemistry
- Determine the significant components
  - List the major species, and focus on those that furnish H^+ ions
    - **Major species**: Solution components that are available in large amounts

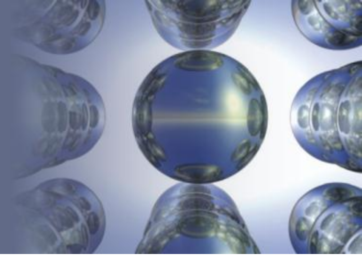
Interactive Example 14.7 - pH of Strong Acids

a. Calculate the pH of 0.10 M HNO_3
b. Calculate the pH of 1.0×10^{-10} M HCl

Interactive Example 14.7 - Solution (a)

- Since HNO_3 is a strong acid, the major species in solution are H^+, NO_3^-, and H_2O
- The concentration of HNO_3 is virtually zero, since the acid completely dissociates in water
    - Also, $[OH^-]$ will be very small because the H^+ ions from the acid will drive the equilibrium to the left

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



Interactive Example 14.7 - Solution (a) (Continued 1)

- This is an acidic solution where $[H^+] >> [OH^-]$, so $[OH^-] << 10^{-7}$ *M* and the sources of H^+ are:
    - H^+ from HNO_3 (0.10 *M*)
    - H^+ from H_2O
    - The number of H^+ ions contributed by the autoionization of water will be very small compared with the 0.10 *M* contributed by the HNO_3 and can be neglected

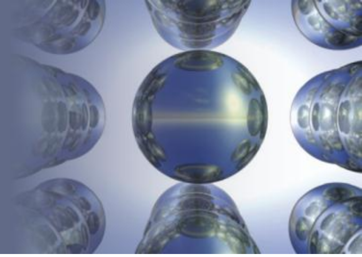
Interactive Example 14.7 - Solution (a) (Continued 2)

- Since the dissolved HNO_3 is the only important source of H^+ ions in this solution,

$$[H^+] = 0.10\ M$$

and

$$pH = -\log(0.10) = 1.00$$



Interactive Example 14.7 - Solution (b)

- Normally, in an aqueous solution of HCl the major species are H^+, Cl^-, and H_2O
    - However, in this case the amount of HCl in solution is so small that it has no effect
        - The only major species is H_2O
    - Thus, the pH will be that of pure water, or pH = 7.00

Problem-Solving Strategy - Solving Weak Acid Equilibrium Problems

1. List the major species in the solution
2. Choose the species that can produce H^+
   - Write balanced equations for the reactions producing H^+
3. Using the values of the equilibrium constants for the reactions, decide which equilibrium will dominate in producing H^+

Problem-Solving Strategy - Solving Weak Acid Equilibrium Problems (Continued 1)

4. Write the equilibrium expression for the dominant equilibrium
5. List the initial concentrations of the species participating in the dominant equilibrium
6. Define the change needed to achieve equilibrium
    - Define x
7. Write the equilibrium concentrations in terms of x

Problem-Solving Strategy - Solving Weak Acid Equilibrium Problems (Continued 2)

8. Substitute the equilibrium concentrations into the equilibrium expression
9. Solve for *x* the easy way
    - Assume that $[\mathrm{HA}]_0 - x \approx [\mathrm{HA}]_0$
10. Use the 5% rule to verify whether the approximation is valid
11. Calculate $[H^+]$ and pH

Critical Thinking

- Consider two aqueous solutions of different weak acids, HA and HB
    - What if all you know about the two acids is that the K_a value for HA is greater than that for HB?
        - Can you tell which of the acids is stronger than the other?
        - Can you tell which of the acid solutions has the lower pH?
        - Defend your answers

Interactive Example 14.8 - The pH of Weak Acids

- The hypochlorite ion (OCl^-) is a strong oxidizing agent often found in household bleaches and disinfectants
  - It is also the active ingredient that forms when swimming-pool water is treated with chlorine
  - In addition to its oxidizing abilities, the hypochlorite ion has a relatively high affinity for protons (it is a much stronger base than Cl^-, for example)

Interactive Example 14.8 - The pH of Weak Acids

(Continued)

- It also forms the weakly acidic hypochlorous acid (HOCl, K_a = 3.5×10^{-8})
- Calculate the pH of a 0.100-*M* aqueous solution of hypochlorous acid

Interactive Example 14.8 - Solution

1. We list the major species
   - Since HOCl is a weak acid and remains mostly undissociated, the major species in a 0.100-*M* HOCl solution are HOCl and H_2O
2. Both species can produce H^+

$$\mathrm{HOCl}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{OCl}^-(aq) \quad K_\mathrm{a} = 3.5 \times 10^{-8}$$

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{OH}^-(aq) \quad K_\mathrm{w} = 1.0 \times 10^{-14}$$

Interactive Example 14.8 - Solution (Continued 1)

3. Since HOCl is a significantly stronger acid than H_2O, it will dominate in the production of H^+
4. We therefore use the following equilibrium expression:

$$K_a = 3.5 \times 10^{-8} = \frac{\left[H^+\right]\left[OCl^-\right]}{[HOCl]}$$

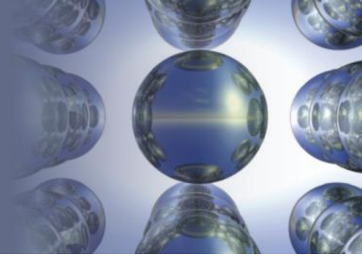
Interactive Example 14.8 - Solution (Continued 2)

5. The initial concentrations appropriate for this equilibrium are

$$[\mathrm{HOCl}]_0 = 0.100\ M$$

$$[\mathrm{OCl^-}]_0 = 0$$

$$[\mathrm{H^+}]_0 \approx 0$$ (We neglect the contribution from H_2O)



Interactive Example 14.8 - Solution (Continued 3)

6. Since the system will reach equilibrium by the dissociation of HOCl, let *x* be the amount of HOCl (in mol/L) that dissociates in reaching equilibrium
7. The equilibrium concentrations in terms of *x* are

$$[\mathrm{HOCl}] = [\mathrm{HOCl}]_0 - x = 0.100 - x$$

$$[\mathrm{OCl}^-] = [\mathrm{OCl}^-]_0 + x = 0 + x = x$$

$$[\mathrm{H}^+] = [\mathrm{H}^+]_0 + x \approx 0 + x = x$$

Interactive Example 14.8 - Solution (Continued 4)

8. Substituting these concentrations into the equilibrium expression gives

$$K_a = 3.5 \times 10^{-8} = \frac{(x)(x)}{0.100 - x}$$

9. Since K_a is so small, we can expect a small value for *x*
    - Thus, we make the approximation $[HA]_0 - x \approx [HA]_0$, or $0.100 - x \approx 0.100$

Interactive Example 14.8 - Solution (Continued 5)

- This leads to the following expression:

$$K_a = 3.5 \times 10^{-8} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

- Solving for *x* gives

$$x = 5.9 \times 10^{-5}$$

10. The approximation $0.100 - x \approx 0.100$ must be validated

Interactive Example 14.8 - Solution (Continued 6)

- To do this, we compare *x* to $[\text{HOCl}]_0$:

$$\frac{x}{[\text{HA}]_0} \times 100 = \frac{x}{[\text{HOCl}]_0} \times 100 = \frac{5.9 \times 10^{-5}}{0.100} \times 100 = 0.059\%$$

  - Since this value is much less than 5%, the approximation is considered valid

11. We calculate $[\text{H}^+]$ and pH

$$[\text{H}^+] = x = 5.9 \times 10^{-5}\ M \text{ and pH} = 4.23$$

Exercise

- What are the major species present in 0.250 *M* solutions of each of the following acids?
  - Calculate the pH of each of these solutions

a. HNO_2

Major species - HNO_2 and H_2O
pH = 2.00

b. CH_3CO_2H ($HC_2H_3O_2$)

Major species - $HC_2H_3O_2$ and H_2O
pH = 2.68

Interactive Example 14.9 - The pH of Weak Acid Mixtures

- Calculate the pH of a solution that contains 1.00 M HCN ($K_a = 6.2 \times 10^{-10}$) and 5.00 M HNO_2 ($K_a = 4.0 \times 10^{-4}$)
  - Also calculate the concentration of cyanide ion (CN^-) in this solution at equilibrium

Interactive Example 14.9 - Solution

- Since HCN and HNO_2 are both weak acids and are largely undissociated, the major species in the solution are HCN, HNO_2, and H_2O
  - All three of these components produce H^+

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{CN}^-(aq) \qquad K_\mathrm{a} = 6.2 \times 10^{-10}$$

$$\mathrm{HNO_2}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{NO_2^-}(aq) \qquad K_\mathrm{a} = 4.0 \times 10^{-4}$$

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{OH}^-(aq) \qquad K_\mathrm{w} = 1.0 \times 10^{-14}$$

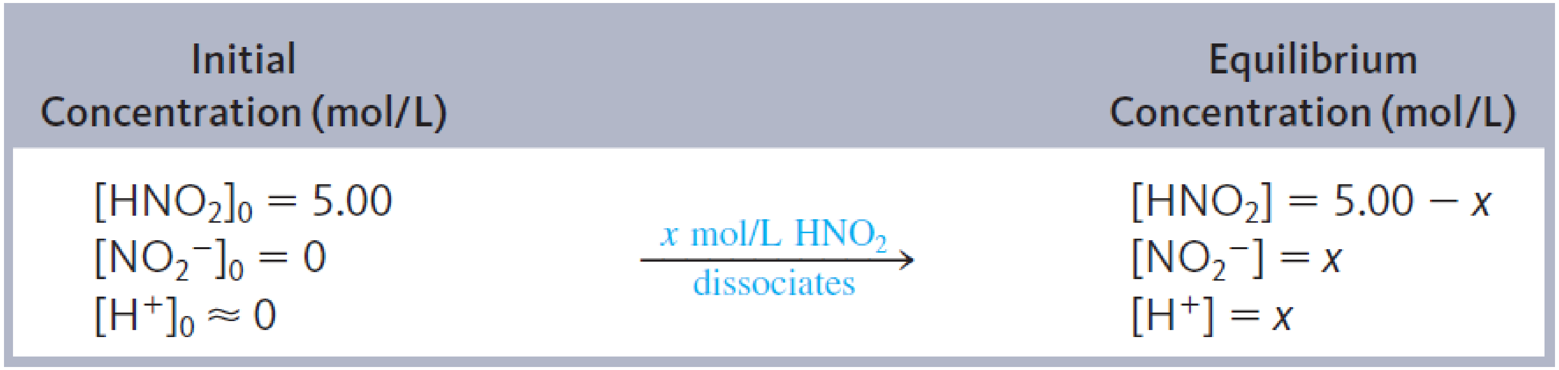
Interactive Example 14.9 - Solution (Continued 1)

- A mixture of three acids might lead to a very complicated problem
  - However, the situation is greatly simplified by the fact that even though HNO_2 is a weak acid, it is much stronger than the other two acids present (as revealed by the *K* values)
    - Thus, HNO_2 can be assumed to be the dominant producer of H^+, and we will focus on its equilibrium expression

Interactive Example 14.9 - Solution (Continued 2)

$$K_a = 4.0 \times 10^{-4} = \frac{[H^+][NO_2^-]}{[HNO_2]}$$

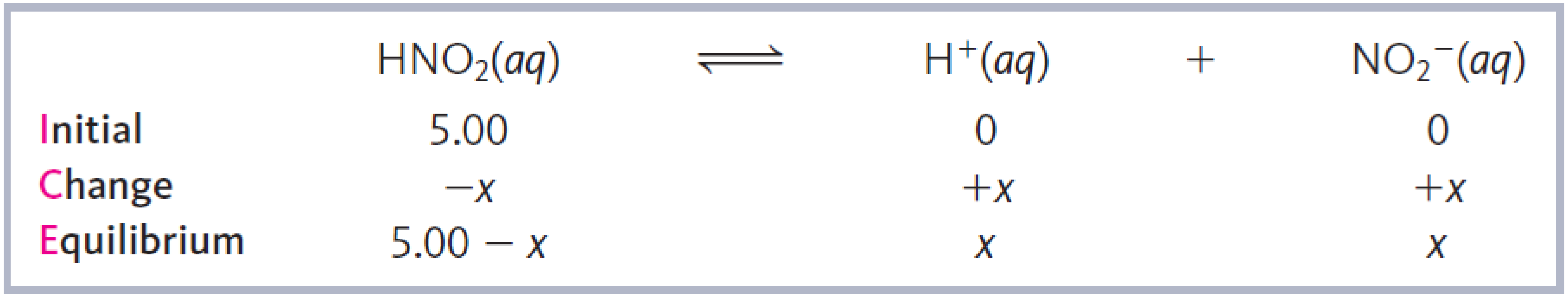
- The initial concentrations, the definition of *x*, and the equilibrium concentrations are as follows:



Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[HNO_2]_0 = 5.00$		$[HNO_2] = 5.00 - x$
$[NO_2^-]_0 = 0$	$\xrightarrow[\text{dissociates}]{x \text{ mol/L } HNO_2}$	$[NO_2^-] = x$
$[H^+]_0 \approx 0$		$[H^+] = x$

Interactive Example 14.9 - Solution (Continued 3)

- It is convenient to represent these concentrations in the following shorthand form (called an ICE table):



	$HNO_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$NO_2^-(aq)$
Initial	5.00		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$5.00 - x$		x		x

- Substitute the equilibrium concentrations in the equilibrium expression

Interactive Example 14.9 - Solution (Continued 4)

- Make the approximation that $5.00 - x = 5.00$

$$K_a = 4.0 \times 10^{-4} = \frac{(x)(x)}{5.00 - x} \approx \frac{x^2}{5.00}$$

  - We solve for *x*:

$$x = 4.5 \times 10^{-2}$$

- Using the 5% rule, we show that the approximation is valid

$$\frac{x}{[\mathrm{HNO_2}]_0} \times 100 = \frac{4.5 \times 10^{-2}}{5.00} \times 100 = 0.90\%$$

Interactive Example 14.9 - Solution (Continued 5)

- Therefore,

$$[\mathrm{H}^+] = x = 4.5 \times 10^{-2}\ M \text{ and } \mathrm{pH} = 1.35$$

- We also want to calculate the equilibrium concentration of cyanide ion in this solution
  - The CN^- ions in this solution come from the dissociation of HCN

$$\mathrm{HCN}(aq) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{CN}^-(aq)$$

Interactive Example 14.9 - Solution (Continued 6)

- Although the position of this equilibrium lies far to the left and does not contribute significantly to $[H^+]$, HCN is the only source of CN^-
  - Thus, we must consider the extent of the dissociation of HCN to calculate $[CN^-]$
- The equilibrium expression for the preceding reaction is

$$K_a = 6.2 \times 10^{-10} = \frac{\left[H^+\right]\left[CN^-\right]}{\left[HCN\right]}$$

Interactive Example 14.9 - Solution (Continued 7)

- We know [H^+] for this solution from the results of the first part of the problem
  - It is important to understand that there is only one kind of H^+ in this solution
- It does not matter from which acid the H^+ ions originate
  - The equilibrium [H^+] we need to insert into the HCN equilibrium expression is 4.5×10^{-2} *M*, even though the H^+ was contributed almost entirely from the dissociation of HNO_2

Interactive Example 14.9 - Solution (Continued 8)

- What is [HCN] at equilibrium?
  - We know $[\mathrm{HCN}]_0 = 1.00\ M$, and since K_a for HCN is so small, a negligible amount of HCN will dissociate
  - Thus,

$$[\mathrm{HCN}] = [\mathrm{HCN}]_0 - \text{amount of HCN dissociated} \approx [\mathrm{HCN}]_0 = 1.00\ M$$

Interactive Example 14.9 - Solution (Continued 9)

- Since $[H^+]$ and [HCN] are known, we can find $[CN^-]$ from the equilibrium expression:

$$K_a = 6.2 \times 10^{-10} = \frac{\left[H^+\right]\left[CN^-\right]}{\left[HCN\right]} = \frac{\left(4.5 \times 10^{-2}\right)\left[CN^-\right]}{1.00}$$

$$\left[CN^-\right] = \frac{\left(6.2 \times 10^{-10}\right)(1.00)}{4.5 \times 10^{-2}} = 1.4 \times 10^{-8}\, M$$

Interactive Example 14.9 - Solution (Continued 10)

- Note the significance of this result
  - Since $[CN^-] = 1.4 \times 10^{-8}$ *M* and HCN is the only source of CN^-, this means that only 1.4×10^{-8} mol/L of HCN dissociated
    - This is a very small amount compared with the initial concentration of HCN, which is exactly what we would expect from its very small K_a value, and [HCN] = 1.00 *M* as assumed

Percent Dissociation

- Definition

$$\text{Percent dissociation} = \frac{\text{amount dissociated } (\text{mol/L})}{\text{initial concentration } (\text{mol/L})} \times 100\%$$

- For a solution of any weak acid HA:
  - $[H^+]$ decreases as $[HA]_0$ decreases
  - Percent dissociation increases as $[HA]_0$ decreases

Interactive Example 14.10 - Calculating Percent Dissociation

- Calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in 1.00 M of $HC_2H_3O_2$

Interactive Example 14.10 - Solution

- Since acetic acid is a weak acid, the major species in this solution are $HC_2H_3O_2$ and H_2O
  - Both species are weak acids, but acetic acid is a much stronger acid than water
    - Thus, the dominant equilibrium will be

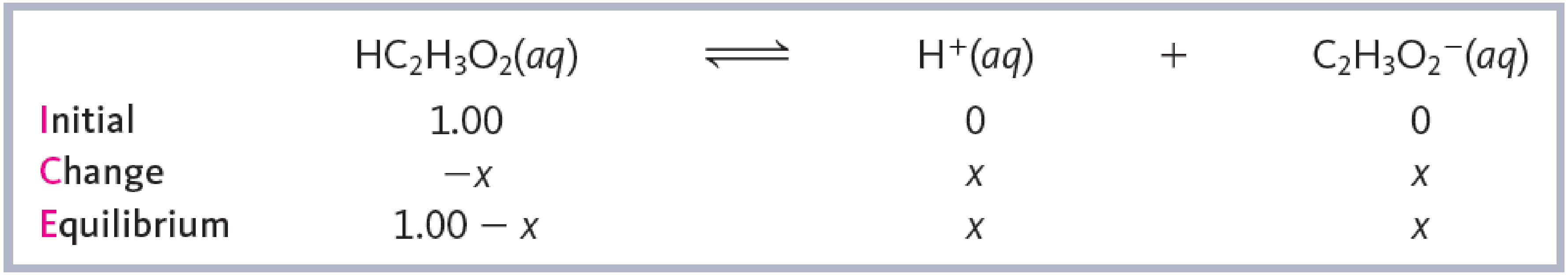
$$\mathrm{HC_2H_3O_2}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{C_2H_3O_2^-}(aq)$$

    - The equilibrium expression is

$$K_\mathrm{a} = 1.8 \times 10^{-5} = \frac{[\mathrm{H^+}][\mathrm{C_2H_3O_2^-}]}{[\mathrm{HC_2H_3O_2}]}$$

Interactive Example 14.10 - Solution (Continued 1)

- The initial concentrations, definition of *x*, and equilibrium concentrations are:



	$HC_2H_3O_2(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$C_2H_3O_2^-(aq)$
Initial	1.00		0		0
Change	$-x$		x		x
Equilibrium	$1.00 - x$		x		x

  - Insert the equilibrium concentrations into the equilibrium expression and make the usual approximation that *x* is small compared with $[HA]_0$

Interactive Example 14.10 - Solution (Continued 2)

$$K_a = 1.8 \times 10^{-5} = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]} = \frac{(x)(x)}{1.00 - x} \approx \frac{x^2}{1.00}$$

- Thus,

$$x^2 \approx 1.8 \times 10^{-5} \text{ and } x \approx 4.2 \times 10^{-3}$$

  - The approximation $1.00 - x \approx 1.00$ is valid by the 5% rule, so

$$[H^+] = x = 4.2 \times 10^{-3}\,M$$

Interactive Example 14.10 - Solution (Continued 3)

- The percent dissociation is

$$\frac{[\mathrm{H}^+]}{[\mathrm{HC_2H_3O_2}]_0} \times 100 = \frac{4.2 \times 10^{-3}}{1.00} \times 100\% = 0.42\%$$

Exercise

- Use Le Châtelier's principle to explain why percent dissociation increases as the concentration of a weak acid decreases

Dilution shifts equilibrium to the side with the greater number of particles (% dissociation increases)

Interactive Example 14.11 - Calculating K_a from Percent Dissociation

- Lactic acid ($HC_3H_5O_3$) is a chemical that accumulates in muscle tissue during exertion
    - In a 0.100-*M* aqueous solution, lactic acid is 3.7% dissociated
        - Calculate the value of K_a for this acid

Interactive Example 14.11 - Solution

- From the small value for the percent dissociation, it is clear that $HC_3H_5O_3$ is a weak acid
  - Thus, the major species in the solution are the undissociated acid and water

$$HC_3H_5O_3 \text{ and } H_2O$$

  - However, even though $HC_3H_5O_3$ is a weak acid, it is a much stronger acid than water and will be the dominant source of H^+ in the solution

Interactive Example 14.11 - Solution (Continued 1)

- The dissociation reaction is

$$HC_3H_5O_3(aq) \rightleftharpoons H^+(aq) + C_3H_5O_3^-(aq)$$

- The equilibrium expression is

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]}$$

Interactive Example 14.11 - Solution (Continued 2)

- The initial and equilibrium concentrations are as follows:

Initial Concentration (mol/L)		Equilibrium Concentration (mol/L)
$[HC_3H_5O_3]_0 = 0.10$		$[HC_3H_5O_3] = 0.10 - x$
$[C_3H_5O_3^-]_0 = 0$	$\xrightarrow[\text{HC}_3\text{H}_5\text{O}_3\text{ dissociates}]{x\text{ mol/L}}$	$[C_3H_5O_3^-] = x$
$[H^+]_0 \approx 0$		$[H^+] = x$

  - The change needed to reach equilibrium can be obtained from the equation of percent dissociation

Interactive Example 14.11 - Solution (Continued 3)

- For this acid,

$$\text{Percent dissociation} = 3.7\% = \frac{x}{[HC_3H_5O_3]_0} \times 100\%$$

$$= \frac{x}{0.10} \times 100\%$$

$$x = \frac{3.7}{100}(0.10) = 3.7 \times 10^{-3} \text{ mol/L}$$

Interactive Example 14.11 - Solution (Continued 4)

- Now we can calculate the equilibrium concentrations:

$[HC_3H_5O_3] = 0.10 - x = 0.10\ M$ (to the correct number of significant figures)

$[C_3H_5O_3^-] = [H^+] = x = 3.7 \times 10^{-3}\ M$

  - These concentrations can now be used to calculate the value of K_a for lactic acid

Interactive Example 14.11 - Solution (Continued 5)

$$K_a = \frac{[H^+][C_3H_5O_3^-]}{[HC_3H_5O_3]} = \frac{(3.7 \times 10^{-3})(3.7 \times 10^{-3})}{0.10}$$

$$K_a = 1.4 \times 10^{-4}$$

Problem-Solving Strategy - Solving Acid–Base Problems

1. List the major species in solution
2. Look for reactions that can be assumed to go to completion
3. For a reaction that can be assumed to go to completion:
    a. Determine the concentration of the products
    b. Write down the major species in solution after the reaction

Problem-Solving Strategy - Solving Acid–Base Problems
(Continued 1)

4. Look at each major component of the solution and decide if it is an acid or a base
5. Pick the equilibrium that will control the pH
    - Use known values of the dissociation constants for the various species to help decide on the dominant equilibrium
        a. Write the equation for the reaction and the equilibrium expression

Problem-Solving Strategy - Solving Acid–Base Problems

(Continued 2)

b. Compute the initial concentrations (assuming the dominant equilibrium has not yet occurred)
c. Define *x*
d. Compute the equilibrium concentrations in terms of *x*
e. Substitute the concentrations into the equilibrium expression, and solve for *x*
f. Check the validity of the approximation
g. Calculate the pH and other concentrations as required

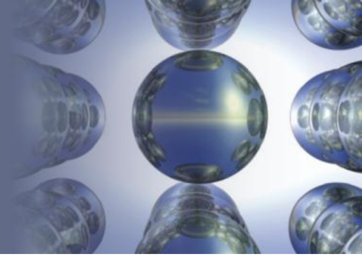
Exercise

- A 0.15-*M* solution of a weak acid is 3.0% dissociated
  - Calculate K_a

$$K_a = 1.4 \times 10^{-4}$$

Strong Bases

- Completely dissociate in water
- Examples
  - Hydroxides of Group 1A elements
  - Alkaline earth hydroxides (Group 2A)



Slaked Lime, $Ca(OH)_2$

- Possesses low solubility
- Used for scrubbing stack gases to remove sulfur dioxide
- Used in water treatment plants
    - **Lime–soda process**: Lime (CaO) and soda ash (Na_2CO_3) are added to hard water in order to soften it

Interactive Example 14.12 - The pH of Strong Bases

- Calculate the pH of a 5.0×10^{-2}-*M* NaOH solution

Interactive Example 14.12 - Solution

- The major species in this solution are Na^+, $OH^–$, and H_2O
- Although autoionization of water also produces $OH^–$ ions, the pH will be dominated by the $OH^–$ ions from the dissolved NaOH
    - Thus, in the solution:

$$[OH^-] = 5.0 \times 10^{-2}\ M$$

Interactive Example 14.12 - Solution (Continued 1)

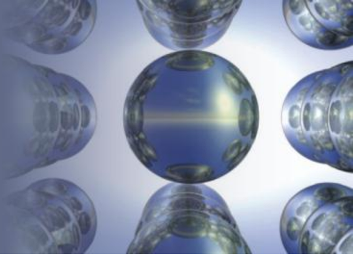
- Concentration of H^+ can be calculated from K_w

$$\left[\mathrm{H}^+\right] = \frac{K_\mathrm{w}}{\left[\mathrm{OH}^-\right]} = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13} M$$

$$\mathrm{pH} = 12.70$$

- Note that this is a basic solution for which

$$[\mathrm{OH}^-] > [\mathrm{H}^+] \text{ and pH} > 7$$



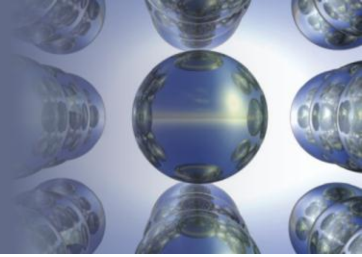
Interactive Example 14.12 - Solution (Continued 2)

- The added OH^- from the salt has shifted the water autoionization equilibrium to the left, significantly lowering $[H^+]$ compared with that in pure water

$$\mathrm{H_2O}(l) \rightleftharpoons \mathrm{H}^+(aq) + \mathrm{OH}^-(aq)$$

Bases in Aqueous Solution

- When bases react with water, they increase the concentration of hydroxide ion
    - Have at least one unshared pair of electrons that is capable of forming a bond with a proton
    - Examples
        - Methylamine
        - Dimethylamine
        - Pyridine



General Reaction and its Equilibrium Constant, K_b

- General reaction between base B and water

$$\mathrm{B}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{BH^+}(aq) + \mathrm{OH^-}(aq)$$

Base Acid Conjugate acid Conjugate base

- Equilibrium constant

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

  - K_b refers to trhe reaction of a base with water to form the conjugate acid and the hydroxide ion
  - **Weak bases**: K_b values are small

Interactive Example 14.14 - The pH of Weak Bases II

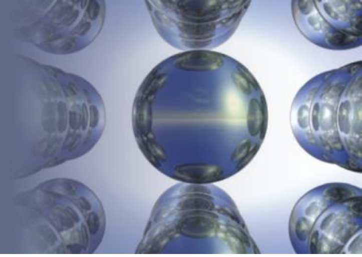
- Calculate the pH of a 1.0-M solution of methylamine ($K_b = 4.38 \times 10^{-4}$)

Interactive Example 14.14 - Solution

- Since methylamine (CH_3NH_2) is a weak base, the major species in solution are CH_3NH_2 and H_2O
    - Both are bases; however, water can be neglected as a source of OH^-, so the dominant equilibrium is

$$\mathrm{CH_3NH_2}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{CH_3NH_3^+}(aq) + \mathrm{OH^-}(aq)$$

$$K_\mathrm{b} = 4.38 \times 10^{-4} = \frac{\left[\mathrm{CH_3NH_3^+}\right]\left[\mathrm{OH^-}\right]}{\left[\mathrm{CH_3NH_2}\right]}$$



Interactive Example 14.14 - Solution (Continued 1)

- The ICE table is:

	$CH_3NH_2(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$CH_3NH_3^+(aq)$	+	$OH^-(aq)$
Initial	1.0		—		0		0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$1.0 - x$		—		x		x

- Substitute the equilibrium concentrations in the equilibrium expression and make the usual approximation

Interactive Example 14.14 - Solution (Continued 2)

$$K_b = 4.38 \times 10^{-4} = \frac{\left[CH_3NH_3^+\right]\left[OH^-\right]}{\left[CH_3NH_2\right]} = \frac{(x)(x)}{1.0 - x} \approx \frac{x^2}{1.0}$$

$$x \approx 2.1 \times 10^{-2}$$

- The approximation is valid by the 5% rule, so

$$[OH^-] = x = 2.1 \times 10^{-2}\ M$$

$$pOH = 1.68$$

$$pH = 14.00 - 1.68 = 12.32$$

Introducing Polyprotic Acids

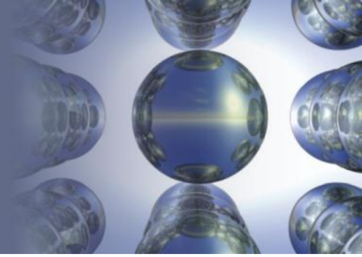
- Acids that can furnish more than one proton
- Dissociate one proton at a time
  - Conjugate base of the first dissociation equilibrium becomes the acid in the second step
- **Triprotic acid**: Have the ability to furnish three protons
  - Example - Phosphoric acid
  - For a typical weak polyprotic acid, $K_{a_1} > K_{a_2} > K_{a_3}$

Introducing Polyprotic Acids (Continued)

  - Loss of second or third proton occurs less readily than the loss of the first proton
  - The positively charged proton cannot be removed easily as the negative charge on the acid increases
- For a typical polyprotic acid in water, only the first dissociation step significantly contributes to $[H^+]$

Interactive Example 14.15 - The pH of a Polyprotic Acid

- Calculate the pH of a 5.0-*M* H_3PO_4 solution and the equilibrium concentrations of the species H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}

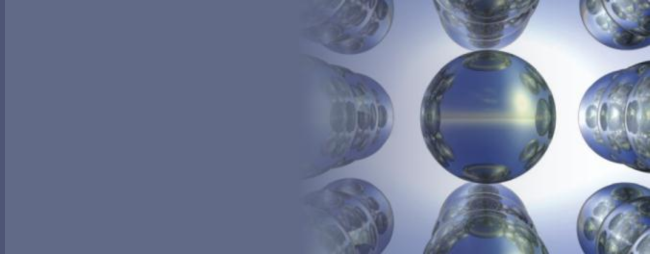


Interactive Example 14.15 - Solution

- The major species in solution are H_3PO_4 and H_2O
- None of the dissociation products of H_3PO_4 is written, since the K_a values are all so small that they will be minor species
  - The dominant equilibrium is the dissociation of H_3PO_4

$$\mathrm{H_3PO_4}(aq) \rightleftharpoons \mathrm{H^+}(aq) + \mathrm{H_2PO_4^-}(aq)$$

$$K_{\mathrm{a}_1} = 7.5 \times 10^{-3} = \frac{[\mathrm{H^+}][\mathrm{H_2PO_4^-}]}{[\mathrm{H_3PO_4}]}$$



Interactive Example 14.15 - Solution (Continued 1)

- The ICE table is:

	$H_3PO_4(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$H_2PO_4^-(aq)$
Initial	5.0		0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$5.0 - x$		x		x

- Substitute the equilibrium concentrations into the expression for K_{a_1} and make the usual approximation

Interactive Example 14.15 - Solution (Continued 2)

$$K_{a_1} = 7.5 \times 10^{-3} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} = \frac{(x)(x)}{5.0 - x} \approx \frac{x^2}{5.0}$$

- Thus, $x \approx 1.9 \times 10^{-1}$
  - Since 1.9×10^{-1} is less than 5% of 5.0, the approximation is acceptable

$$[H^+] = x = 0.19\ M$$

$$\text{pH} = 0.72$$

Interactive Example 14.15 - Solution (Continued 3)

- So far we have determined that

$$[H^+] = [H_2PO_4^-] = 0.19\ M$$

$$[H_3PO_4] = 5.0 - x = 4.8\ M$$

  - The concentration of HPO_4^{2-} can be obtained by using the expression for K_{a_2}

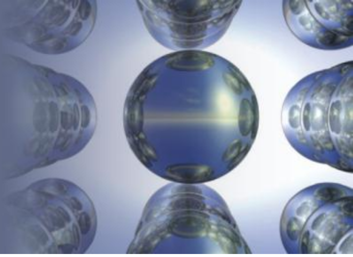
$$K_{a_2} = 6.2 \times 10^{-8} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4]} \text{ where } [H^+] = [H_2PO_4^-] = 0.19M$$

Interactive Example 14.15 - Solution (Continued 4)

  - Thus, $[\mathrm{HPO_4}^{2-}] = K_{\mathrm{a}_2} = 6.2 \times 10^{-8}\ M$
- To calculate $[\mathrm{PO_4}^{3-}]$, we use the expression for K_{a_3} and the values of $[\mathrm{H}^+]$ and $[\mathrm{HPO_4}^{2-}]$ calculated previously:

$$K_{\mathrm{a}_3} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{PO}_4^{3-}\right]}{\left[\mathrm{HPO}_4^{2-}\right]} = 4.8 \times 10^{-13} = \frac{0.19\left[\mathrm{PO}_4^{3-}\right]}{\left(6.2 \times 10^{-8}\right)}$$

$$\left[\mathrm{PO}_4^{3-}\right] = \frac{\left(4.8 \times 10^{-13}\right)\left(6.2 \times 10^{-8}\right)}{0.19} = 1.6 \times 10^{-19} M$$



Interactive Example 14.15 - Solution (Continued 5)

- These results show that the second and third dissociation steps do not make an important contribution to $[H^+]$
  - This is apparent from the fact that $[HPO_4^{2-}]$ is 6.2×10^{-8} *M*, which means that only 6.2×10^{-8} mol/L $H_2PO_4^-$ has dissociated
  - The value of $[PO_4^{3-}]$ shows that the dissociation of HPO_4^{2-} is even smaller
    - We must use the second and third dissociation steps to calculate $[HPO_4^{2-}]$ and $[PO_4^{3-}]$, since these steps are the only sources of these ions

Critical Thinking

- What if the three values of K_a for phosphoric acid were closer to each other in value?
    - Why would this complicate the calculation of the pH for an aqueous solution of phosphoric acid?

Sulfuric Acid - A Unique Polyprotic Acid

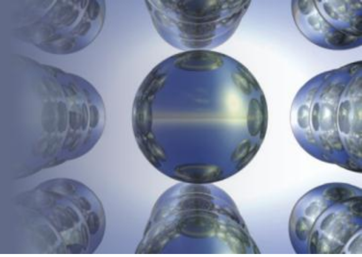
- A strong acid in its first dissociation step and a weak acid in its second step

$$H_2SO_4(aq) \longrightarrow H^+(aq) + HSO_4^-(aq) \quad K_{a_1} \text{ is very large}$$

$$HSO_4^-(aq) \rightleftharpoons H^+(aq) + SO_4^{2-}(aq) \quad K_{a_2} = 1.2 \times 10^{-2}$$

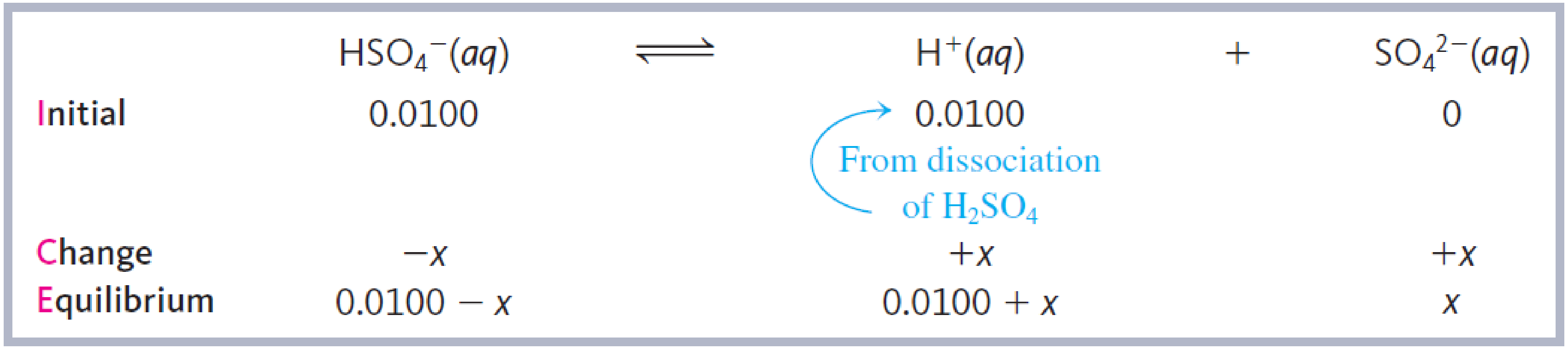
Example 14.17 - The pH of Sulfuric Acid

- Calculate the pH of a 1.00×10^{-2} *M* H_2SO_4 solution

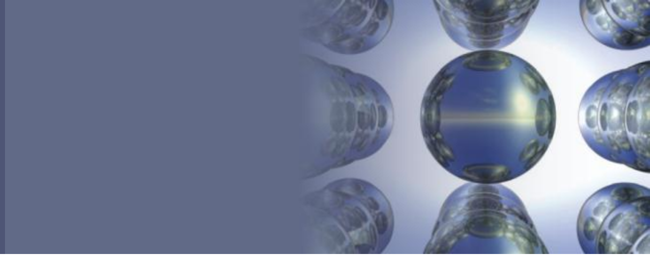


Example 14.17 - Solution

- The major species in solution are H^+, HSO_4^-, and H_2O
- Consider the dissociation of HSO_4^-
    - ICE table



	$HSO_4^-(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$SO_4^{2-}(aq)$
Initial	0.0100		0.0100		0
			From dissociation of H_2SO_4		
Change	$-x$		$+x$		$+x$
Equilibrium	$0.0100 - x$		$0.0100 + x$		x



Example 14.17 - Solution (Continued 1)

- Substitute the equilibrium concentrations into the expression for K_{a_2}

$$1.2 \times 10^{-2} = K_{a_2} = \frac{\left[\mathrm{H}^+\right]\left[\mathrm{SO}_4^{2-}\right]}{\left[\mathrm{HSO}_4^-\right]} = \frac{(0.0100 + x)(x)}{(0.0100 - x)}$$

  - If we make the usual approximation, then $0.0100 + x \approx 0.0100$ and $0.0100 - x \approx 0.0100$, and we have

$$1.2 \times 10^{-2} = \frac{(0.0100 + x)(x)}{(0.0100 - x)} \approx \frac{(0.0100)x}{(0.0100)}$$

Example 14.17 - Solution (Continued 2)

- The calculated value of *x* is

$$x = 1.2 \times 10^{-2} = 0.012$$

  - This value is larger than 0.010, clearly a ridiculous result
  - Thus, we cannot make the usual approximation and must instead solve the quadratic equation

Example 14.17 - Solution (Continued 3)

$$1.2\times10^{-2}=\frac{(0.0100+x)(x)}{(0.0100-x)}$$

- The above expression leads to:

$$(1.2\times10^{-2})(0.0100-x)=(0.0100+x)(x)$$

$$(1.2\times10^{-4})-(1.2\times10^{-2})\,x=(1.0\times10^{-2})\,x+x^2$$

$$x^2+(2.2\times10^{-2})\,x-(1.2\times10^{-4})=0$$

Example 14.17 - Solution (Continued 4)

- This equation can be solved using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

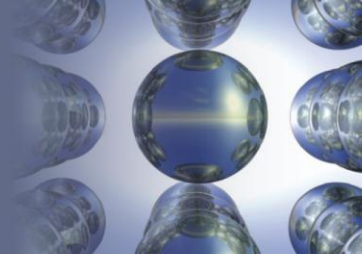
$a = 1$

$b = 2.2 \times 10^{-2}$

$c = -1.2 \times 10^{-4}$

- Use of the quadratic formula gives one negative root (which cannot be correct) and one positive root,

$$x = 4.5 \times 10^{-3}$$



Example 14.17 - Solution (Continued 5)

- Thus,

$$[H^+] = 0.0100 + x = 0.0100 + 0.0045 = 0.0145$$

$$\text{pH} = 1.84$$

- Note that in this case the second dissociation step produces about half as many H^+ ions as the initial step does
    - This problem also can be solved by successive approximations

Salts

- Another name for ionic compounds
- Disintegrate into ions when dissolved in water
  - Have independent movement in dilute solutions
  - Behave as acids or bases under certain conditions

Salts That Produce Neutral Solutions

- When dissolved in water, salts that consist of cations of strong bases and anions of strong acids have no effect on [H^+]
    - Gives a neutral solution (pH = 7)
    - Examples - KCl, NaCl, $NaNO_3$, and KNO_3

Salts That Produce Basic Solutions

- A basic solution is formed if the anion of the salt is the conjugate base of a weak acid
  - K_b value for the anion can be obtained from the relationship

$$K_b = K_w/K_a$$

- Example - Sodium acetate ($NaC_2H_3O_2$)

Interactive Example 14.18 - Salts as Weak Bases

- Calculate the pH of a 0.30-*M* NaF solution
    - The K_a value for HF is 7.2×10^{-4}

Interactive Example 14.18 - Solution

- The major species in solution are Na^+, F^-, and H_2O
- Since HF is a weak acid, the F^- ion must have a significant affinity for protons, and the dominant reaction will be

$$\mathrm{F^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HF}(aq) + \mathrm{OH^-}(aq)$$

  - This yields the following K_b expression:

$$K_b = \frac{[\mathrm{HF}][\mathrm{OH^-}]}{[\mathrm{F^-}]}$$

Interactive Example 14.18 - Solution (Continued 1)

- Value of K_b can be calculated from K_w and the K_a value for HF:

$$K_b = \frac{K_w}{K_a(\text{for HF})} = \frac{1.0 \times 10^{-14}}{7.2 \times 10^{-4}} = 1.4 \times 10^{-11}$$

- The corresponding ICE table is:

	$F^-(aq)$	+	$H_2O(l)$	$\rightleftharpoons$	$HF(aq)$	+	$OH^-(aq)$
Initial	0.30		—		0		≈ 0
Change	$-x$		—		$+x$		$+x$
Equilibrium	$0.30 - x$		—		x		x

Interactive Example 14.18 - Solution (Continued 2)

- Thus,

$$K_b = 1.4 \times 10^{-11} = \frac{[\text{HF}][\text{OH}^-]}{[\text{F}^-]} = \frac{(x)(x)}{0.30-(x)} \approx \frac{x^2}{0.30}$$

$$x \approx 2.0 \times 10^{-6}$$

- The approximation is valid by the 5% rule

Interactive Example 14.18 - Solution (Continued 3)

$$[\mathrm{OH^-}] = x = 2.0 \times 10^{-6}\ M$$

$$\mathrm{pOH} = 5.69$$

$$\mathrm{pH} = 14.00 - 5.69 = 8.31$$

- As expected, the solution is basic

Base Strength in Aqueous Solutions

- Consider the dissociation of hydrocyanic acid in H_2O

$$\mathrm{HCN}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{H_3O^+}(aq) + \mathrm{CN^-}(aq) \quad K_\mathrm{a} = 6.2 \times 10^{-10}$$

  - CN^- appears to be a strong base in this reaction

$$\mathrm{CN^-}(aq) + \mathrm{H_2O}(l) \rightleftharpoons \mathrm{HCN}(aq) + \mathrm{OH^-}(aq)$$

$$K_\mathrm{b} = \frac{K_\mathrm{w}}{K_\mathrm{a}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

Base Strength in Aqueous Solutions (Continued)

- CN^- appears to be a weak base when cyanide ion reacts with water
  - Competes with the hydroxide ion for H^+ instead of competing with water
- Relative base strengths

$$OH^- > CN^- > H_2O$$

Salts That Produce Acidic Solutions

- Salts in which the anion is not a base and the cation is the conjugate acid of a weak base
    - Example - Ammonium chloride (NH_4Cl)
- Salts that contain highly charged metal ions
    - Example - Solid aluminum chloride ($AlCl_3$)
    - Higher the charge on the metal ion, stronger the acidity of the hydrated ion

Interactive Example 14.19 - Salts as Weak Acids I

- Calculate the pH of a 0.10-*M* NH_4Cl solution
    - The K_b value for NH_3 is 1.8×10^{-5}

Interactive Example 14.19 - Solution

- The major species in solution are NH_4^+, Cl^-, and H_2O
  - Note that both NH_4^+ and H_2O can produce H^+
  - The dissociation reaction for the NH_4^+ ion is

$$\mathrm{NH_4^+}(aq) \rightleftharpoons \mathrm{NH_3}(aq) + \mathrm{H^+}(aq)$$

$$K_\mathrm{a} = \frac{[\mathrm{NH_3}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]}$$

Interactive Example 14.19 - Solution (Continued 1)

- Note that although the K_b value for NH_3 is given, the reaction corresponding to K_b is not appropriate here, since NH_3 is not a major species in the solution
    - Instead, the given value of K_b is used to calculate K_a for NH_4^+ from the relationship

$$K_a \times K_b = K_w$$

Interactive Example 14.19 - Solution (Continued 2)

- Thus,

$$K_a\left(\text{for NH}_4^+\right) = \frac{K_w}{K_b\left(\text{for NH}_3\right)} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

- Although NH_4^+ is a very weak acid, as indicated by its K_a value, it is stronger than H_2O and will dominate in the production of H^+
    - Thus, we will focus on the dissociation reaction of NH_4^+ to calculate the pH in this solution

Interactive Example 14.19 - Solution (Continued 3)

	$NH_4^+(aq)$	$\rightleftharpoons$	$H^+(aq)$	$+$	$NH_3(aq)$
Initial	0.10		≈ 0		0
Change	$-x$		$+x$		$+x$
Equilibrium	$0.10 - x$		x		x

- Thus,

$$5.6 \times 10^{-10} = K_a = \frac{[H^+][NH_3]}{[NH_4^+]} = \frac{(x)(x)}{0.10 - x} \approx \frac{x^2}{0.10}$$

$$x \approx 7.5 \times 10^{-6}$$

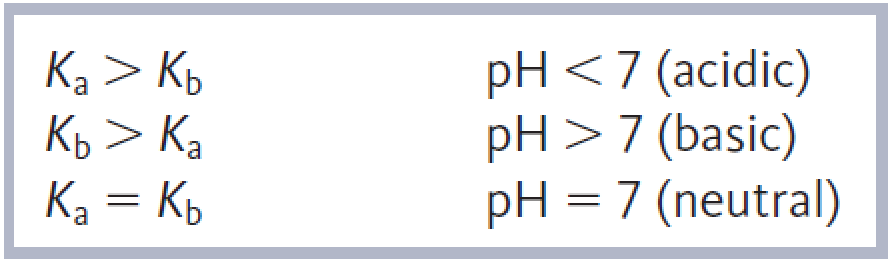
Interactive Example 14.19 - Solution (Continued 4)

- The approximation is valid by the 5% rule, so

$$[\mathrm{H^+}] = x = 7.5 \times 10^{-6}\ M$$

$$\mathrm{pH} = 5.13$$

Table 14.5 - Qualitative Prediction of pH for Solutions of Salts

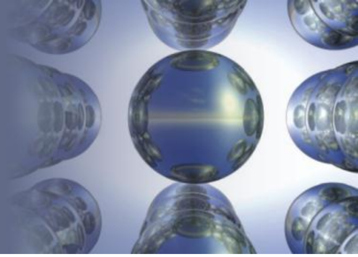


$K_a > K_b$	pH < 7 (acidic)
$K_b > K_a$	pH > 7 (basic)
$K_a = K_b$	pH = 7 (neutral)

Both cation and anion have acidic or basic properties

Interactive Example 14.21 - The Acid–Base Properties of Salts

- Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral
  a. $NH_4C_2H_3O_2$
  b. NH_4CN



Interactive Example 14.21 - Solution (a)

- The ions in solution are NH_4^+ and $C_2H_3O_2^-$
- K_a for NH_4^+ is 5.6×10^{-10}
- K_b for $C_2H_3O_2^-$ is 5.6×10^{-10}
    - Thus, K_a for NH_4^+ is equal to K_b for $C_2H_3O_2^-$, and the solution will be neutral (pH = 7)

Interactive Example 14.21 - Solution (b)

- The solution will contain NH_4^+ and CN^- ions
  - The K_a value for NH_4^+ is 5.6×10^{-10} and

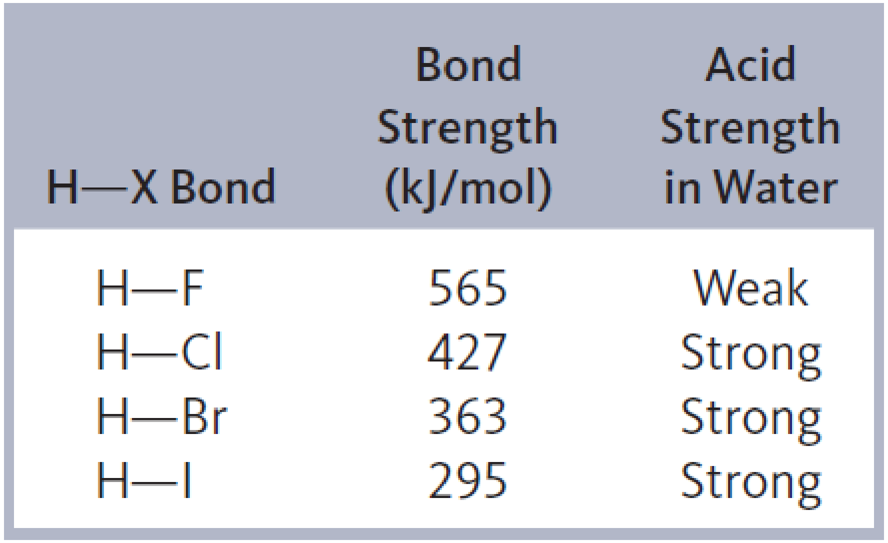
$$K_b\left(\text{for CN}^-\right) = \frac{K_w}{K_a\left(\text{for HCN}\right)} = 1.6 \times 10^{-5}$$

  - Since K_b for CN^- is much larger than K_a for NH_4^+, CN^- is a much stronger base than NH_4^+ is an acid
  - The solution will be basic

Acids and Bases

- Factors that determine whether a molecule containing an X—H bond behaves as a Brønsted–Lowry acid
  - Bond strength
  - Bond polarity
- Classes of acids - Hydrogen halides, oxyacids, and hydrated metal ions

Table 14.7 - Bond Strengths and Acid Strengths for Hydrogen Halides



H—X Bond	Bond Strength (kJ/mol)	Acid Strength in Water
H—F	565	Weak
H—Cl	427	Strong
H—Br	363	Strong
H—I	295	Strong

Oxyacids

- Contain the grouping H—O—X
- For a given series, the acid strength increases with an increase in the number of oxygen atoms attached to the central atom
- Acid strength is successively greater as the number of oxygen atoms increases
    - Oxygen atoms become more effective at drawing electrons away from the X atom and the O—H bond
        - Weaken and polarize the O—H bond

Table 14.8 - Several Series of Oxyacids and Their K_a Values

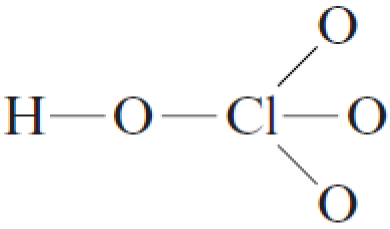
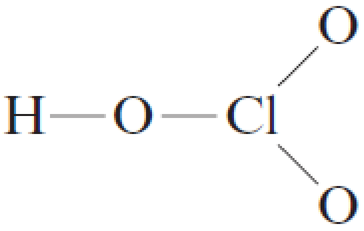
Oxyacid	Structure	K_a Value
$HClO_4$		Large ($\sim 10^7$)
$HClO_3$		~ 1
$HClO_2$	H—O—Cl—O	1.2×10^{-2}
HClO	H—O—Cl	3.5×10^{-8}

Table 14.8 - Several Series of Oxyacids and Their K_a Values (Continued)

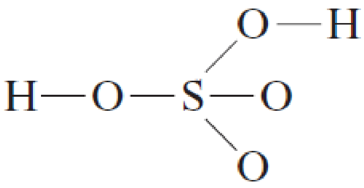
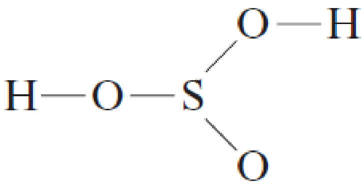
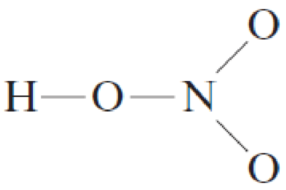
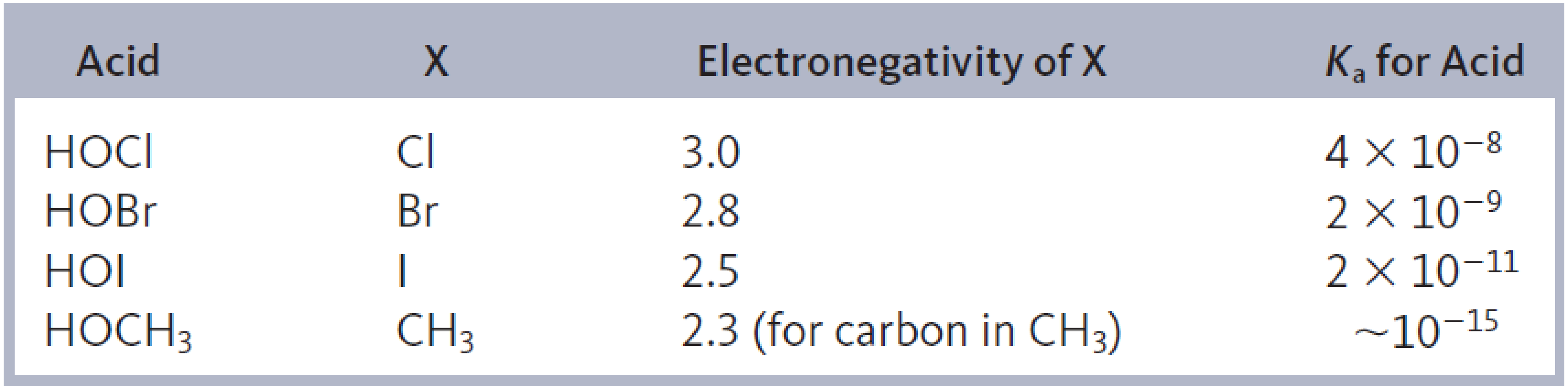
Oxyacid	Structure	K_a Value
H_2SO_4		Large
H_2SO_3		1.5×10^{-2}
HNO_3		Large
HNO_2	H—O—N—O	4.0×10^{-4}

Table 14.9 - Comparison of Electronegativity of X and K_a Value for a Series of Oxyacids



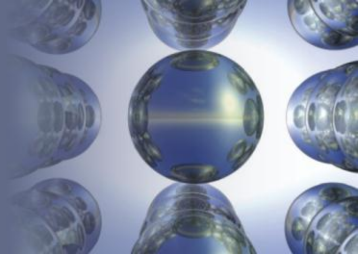
Acid	X	Electronegativity of X	K_a for Acid
HOCl	Cl	3.0	4×10^{-8}
HOBr	Br	2.8	2×10^{-9}
HOI	I	2.5	2×10^{-11}
$HOCH_3$	CH_3	2.3 (for carbon in CH_3)	$\sim 10^{-15}$

Hydrated Metal Ions

- Exhibit behavior similar to oxyacids
- Greater the charge on the metal ion, more acidic the hydrated ion becomes

Acidic Strength in Oxides

- A compound containing the H—O—X group will produce:
    - An acidic solution in water if the O—X bond is strong and covalent
    - A basic solution in water if the O—X bond is ionic
- High electronegativity of X will lead to covalent and strong O—X bond
    - Low electronegativity will lead to ionic and weak O—X bond



Acidic Oxides

- Formed when covalent oxides are dissolved in water
  - Leads to the formation of an acidic solution
  - O—X bond remains intact
- Examples - SO_2, CO_2, and NO_2

Basic Oxides

- Ionic oxides dissolve in water to form basic solutions
- Examples - K_2O and CaO
    - Oxide ion has a high affinity for protons and reacts with water to produce hydroxide ions

Lewis Acids and Bases

- **Lewis acid**: Electron-pair acceptor
    - Contains an empty atomic orbital that can be used to accept an electron pair from the Lewis base
- **Lewis base**: Electron-pair donor

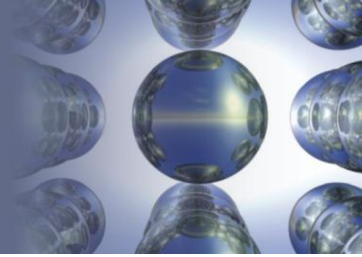
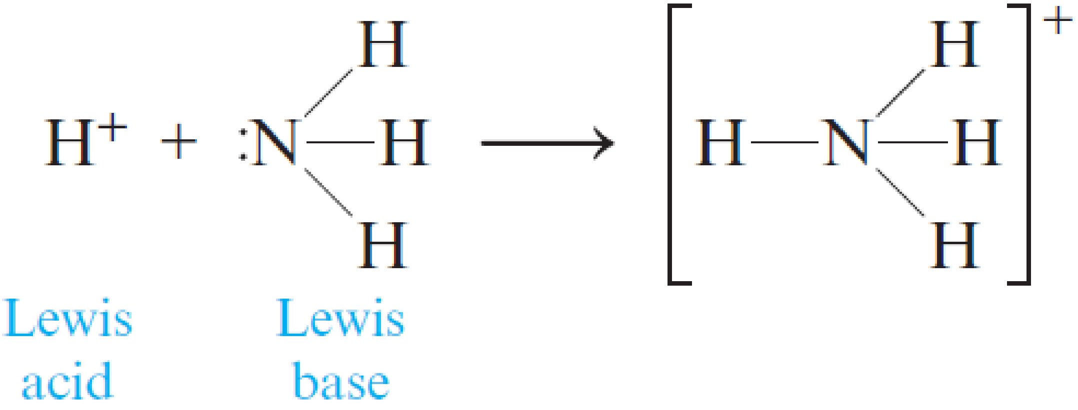


Table 14.10 - Three Models for Acids and Bases

Model	Definition of Acid	Definition of Base
Arrhenius	H^+ producer	OH^- producer
Brønsted–Lowry	H^+ donor	H^+ acceptor
Lewis	Electron-pair acceptor	Electron-pair donor

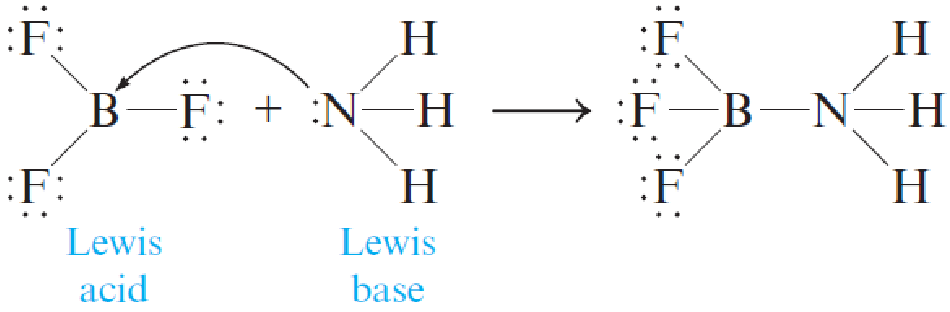
The Lewis Model and Brønsted–Lowry Acid–Base Reactions

- Reaction between a proton and an NH_3 molecule can be represented as a reaction between an electron pair acceptor (H^+) and electron-pair donor (NH_3)



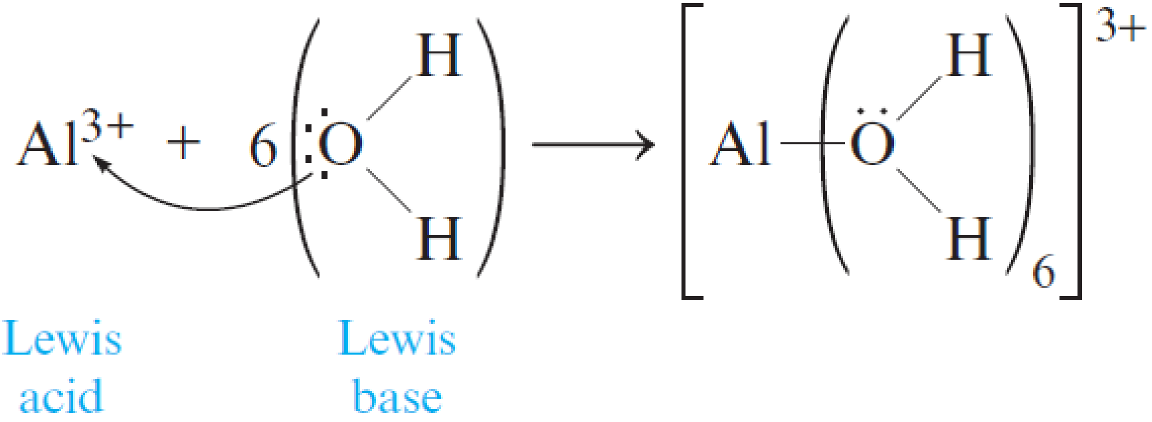
The Lewis Model and Other Reactions

- Lewis model for acids and bases covers many reactions that do not involve Brønsted–Lowry acids
  - Example - Gas-phase reaction between boron trifluoride and ammonia
    - Electron-deficient BF_3 molecule completes its octet by reacting with NH_3, which has a lone pair of electrons



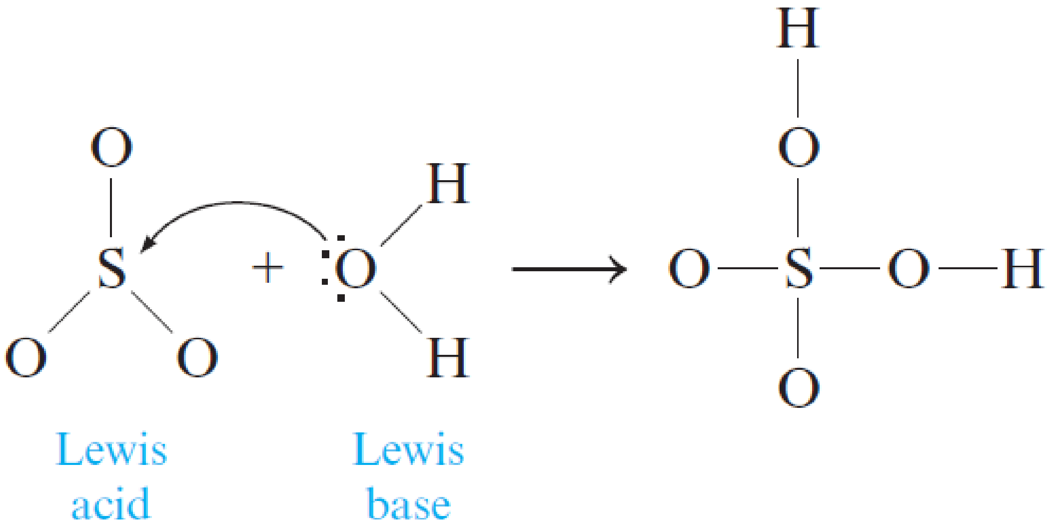
The Lewis Model and Other Reactions (Continued 1)

- Example - Hydration of a metal ion, Al^{3+}
  - Ion accepts one electron pair from each of the water molecules to form the complex ion $Al(H_2O)_6^{3+}$



The Lewis Model and Other Reactions (Continued 2)

- Reaction between a covalent oxide and water
  - Example - Reaction between sulfur trioxide and water
    - Proton shift leads to the formation of sulfuric acid



Example 14.22 - Lewis Acids and Bases

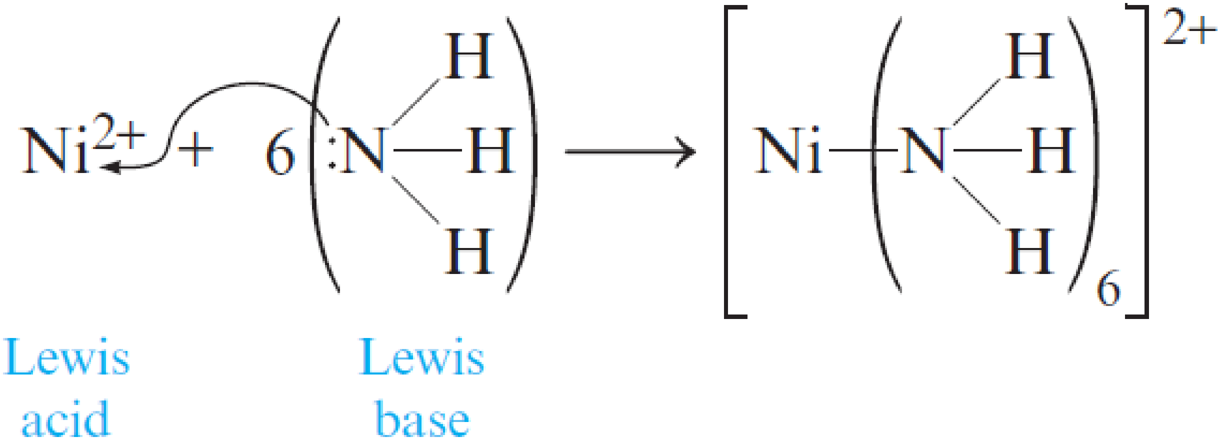
- For each reaction, identify the Lewis acid and base

a. $\mathrm{Ni}^{2+}(aq) + 6\mathrm{NH}_3(aq) \longrightarrow \mathrm{Ni}(\mathrm{NH}_3)_6^{2+}(aq)$

b. $\mathrm{H}^{+}(aq) + \mathrm{H}_2\mathrm{O}(aq) \rightleftharpoons \mathrm{H}_3\mathrm{O}^{+}(aq)$

Example 14.22 - Solution (a)

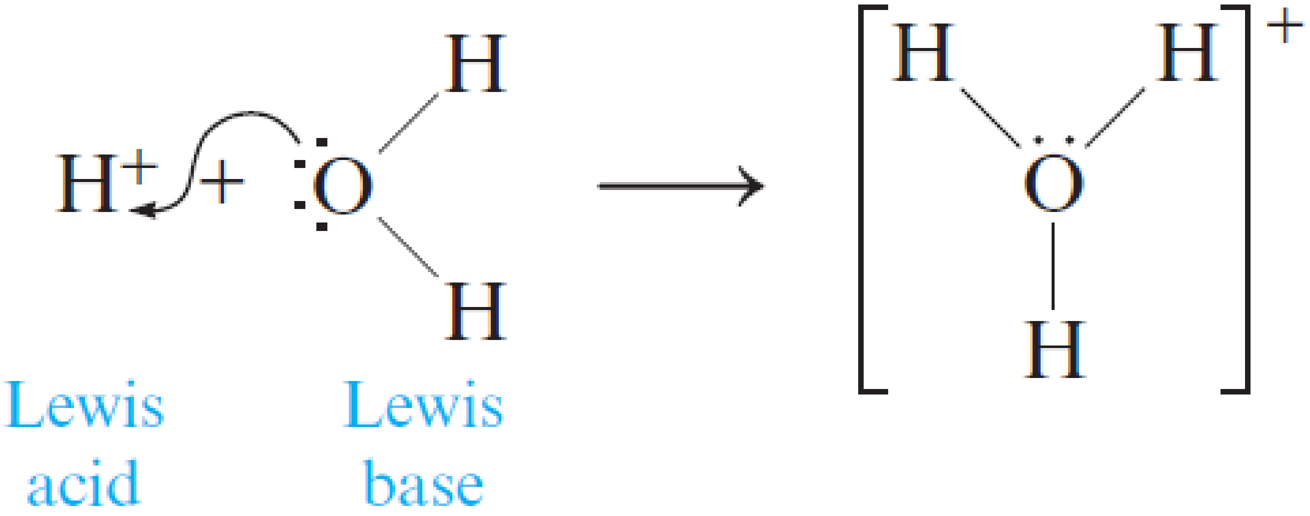
- Each NH_3 molecule donates an electron pair to the Ni^{2+} ion:



  - The nickel(II) ion is the Lewis acid, and ammonia is the Lewis base

Example 14.22 - Solution (b)

- The proton is the Lewis acid and the water molecule is the Lewis base



Analyzing an Acid–Base Equilibrium Problem

- Analysis done at the beginning of the problem is imperative
  - Note the major species present in the solution
  - Determine if the reaction will go to completion
  - Ascertain the equilibrium that dominates the solution