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Chapter 13 Acids and Bases

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Brønsted-Lowry Acid-Base Model

- Brønsted-Lowry
 - Johannes Brønsted (1879-1947)
 - Thomas Lowry (1874-1936)
- Brønsted-Lowry model focuses on the **reaction that takes place between acid and base**, rather than on the independent nature of the acid or base, as the Arrhenius model does
 - Acids donate H^+ to bases
 - Bases accept H^+ from acids

Outline

1. Brønsted-Lowry acid-base model
2. The ion product of water
3. pH and pOH
4. Weak acids and their equilibrium constants
5. Weak bases and their equilibrium constants
6. Acid-base properties of salt solutions
7. Extending the concept of acids and bases: the Lewis model

The Nature of H^+

- The H^+ ion is the medium of exchange in a Brønsted-Lowry reaction
 - H^+ can also be called a proton
 - **Acid-base reactions involve proton exchange**

Review from Chapter 4

- The Arrhenius definition of acid and base
 - Acids produce H^+ in water
 - Bases produce OH^- in water
 - H^+ from acids combines with OH^- from bases to produce water in a reaction called a neutralization

Conjugate Pairs

- The species that forms when a proton is removed from an acid is called the **conjugate base** of the acid
 - If the acid is HB , the conjugate base is B^-
- The only difference between the members of a conjugate acid-base pair is the position of the proton
- A species that can either accept or donate a proton is called amphiprotic
 - Consider water:
 - $OH^- \leftarrow H_2O \rightarrow H_3O^+$
 - Remove H^+ Add H^+

Examples of Conjugate Acid-Base Pairs

Conjugate Acid	Conjugate Base
HF	F ⁻
HSO ₄ ⁻	SO ₄ ²⁻
NH ₄ ⁺	NH ₃

Example 13.1, (Cont'd)

SOLUTION	
(a) HNO ₂ conjugate base	HNO ₂ → NO ₂ ⁻¹ → NO ₂ ⁻
F ⁻ conjugate acid	F ⁻ → HF ⁻¹⁺¹ → HF
(b) HCO ₃ ⁻ conjugate base	HCO ₃ ⁻ → CO ₃ ⁻¹⁻¹ → CO ₃ ²⁻
HCO ₃ ⁻ conjugate acid	HCO ₃ ⁻ → H ₂ CO ₃ ⁻¹⁺¹ → H ₂ CO ₃

The Hydronium Ion

- Another way to write the H⁺ ion is as H₃O⁺
 - H₃O⁺ is the hydronium ion
 - H⁺ exists in water as hydronium ion, since H⁺ itself would not be stable in water
- Depending on the reason for writing the reaction, either H⁺ or H₃O⁺ can be used, and interchangeably
- The only difference is the inclusion or exclusion of the H₂O molecule

The Ion Product of Water

- Water can react with itself in a reaction called **autoionization**
- Water can react with itself in an acid-base reaction:
 - H₂O + H₂O ⇌ H₃O⁺ (aq) + OH⁻ (aq)
- An alternate way to write the reaction is:
 - H₂O ⇌ H⁺ (aq) + OH⁻ (aq)

Example 13.1

EXAMPLE 13.1

- (a) What is the conjugate base of HNO₂? The conjugate acid of F⁻?
 (b) The HCO₃⁻ ion, like the H₂O molecule, is amphiprotic. What is its conjugate base? Its conjugate acid?

STRATEGY

1. Form the conjugate base by removing one H atom. Decrease the charge by one unit (e.g., -1 to -2).
2. Form the conjugate acid by adding one H atom. Increase the charge by one unit (e.g., -1 to 0).

continued

Equilibrium and the Auto-Ionization of Water

- H₂O ⇌ H⁺ (aq) + OH⁻ (aq)
 - Recall that concentrations can be used to write equilibrium constant expressions
 - K for this reaction is [H⁺][OH⁻]
 - This K is called the **ion product constant of water, K_w**
 - K_w = [H⁺][OH⁻]
 - At 25 °C, K_w = 1.0 × 10⁻¹⁴

Concentrations of H⁺ and OH⁻ in pure water

- For water, $[H^+][OH^-] = 1.0 \times 10^{-14}$
- In pure water, the two concentrations are equal:
 - $[H^+] = 1.0 \times 10^{-7} \text{ M}$
 - $[OH^-] = 1.0 \times 10^{-7} \text{ M}$
- Since one concentration must rise as the other falls,
 - If $[H^+] > 1.0 \times 10^{-7} \text{ M}$, then $[OH^-] < 1.0 \times 10^{-7} \text{ M}$ and the solution is acidic
 - If $[OH^-] > 1.0 \times 10^{-7} \text{ M}$, then $[H^+] < 1.0 \times 10^{-7} \text{ M}$ and the solution is basic

Figure 13.2

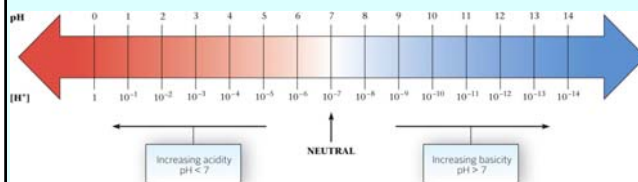
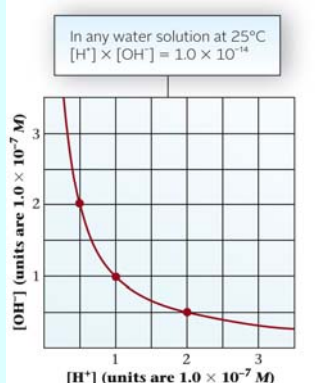


Figure 13.1



pOH

- Defining equation for pH

$$pOH = -\log[OH^-]$$

$$[OH^-] = \text{antilog}[-pOH] = 10^{-pOH}$$

- The higher the pOH, the more basic the solution
- The lower the pOH, the more acidic the solution

pH

- Defining equation for pH

$$pH = -\log[H^+]$$

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

- The higher the pH, the less acidic the solution
- The lower the pH, the more acidic the solution

Relationship between pH and pOH

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

$$pH + pOH = 14.00$$

Table 13.1: pH of Some Common Materials

TABLE 13.1 pH of Some Common Materials

Lemon juice	2.2–2.4	Urine, human	4.8–8.4
Wine	2.8–3.8	Cow's milk	6.3–6.6
Vinegar	3.0	Saliva, human	6.5–7.5
Tomato juice	4.0	Drinking water	5.5–8.0
Beer	4–5	Blood, human	7.3–7.5
Cheese	4.8–6.4	Seawater	8.3

Example 13.2, (Cont'd)

ANALYSIS	
Information given:	$[H^+]$ and $[OH^-]$ relation ($[H^+] = 5.0 [OH^-]$)
Information implied:	K_w value
Asked for:	pOH
STRATEGY	
1. Substitute into Equation 13.1 to obtain $[OH^-]$.	
2. Substitute into Equation 13.4 to convert $[OH^-]$ to pOH.	
SOLUTION	
1. $[OH^-]$	$1.0 \times 10^{-14} = [OH^-][H^+] = [OH^-](5.0[OH^-]) = 5.0[OH^-]^2$ $[OH^-]^2 = \frac{1.0 \times 10^{-14}}{5.0} \rightarrow [OH^-] = 4.5 \times 10^{-8} M$
2. pOH	$pOH = -\log_{10}[OH^-] = -\log_{10}(4.5 \times 10^{-8}) = 7.35$

Example 13.2

EXAMPLE 13.2 GRADED

Calculate, at 25°C:

- the $[H^+]$ and pH of a tapwater sample in which $[OH^-] = 2.0 \times 10^{-7}$,
- the $[H^+]$ and $[OH^-]$ of human blood at pH 7.40,
- the pOH of a solution in which $[H^+] = (5.0)[OH^-]$.

ANALYSIS	
Information given:	$[OH^-]$ ($2.0 \times 10^{-7} M$)
Information implied:	K_w value
Asked for:	$[H^+]$ and pH
STRATEGY	
1. Substitute into Equation 13.1 to obtain $[H^+]$.	
2. Substitute into Equation 13.3 to convert $[H^+]$ to pH.	
SOLUTION	
1. $[H^+]$	$K_w = 1.0 \times 10^{-14} = [H^+][OH^-] = [H^+](2.0 \times 10^{-7})$ $[H^+] = \frac{1.0 \times 10^{-14}}{2.0 \times 10^{-7}} = 5.0 \times 10^{-8} M$
2. pH	$pH = -\log_{10}[H^+] = -\log_{10}(5.0 \times 10^{-8}) = 7.30$

pH and Blood

- From the previous example, it is seen that the $[H^+]$ in blood is very small, about $4.0 \times 10^{-8} M$
- Small changes in $[H^+]$ can have dramatic physiological effects
 - Many biological reactions depend on $[H^+]$
 - An increase in $[H^+]$ from 4.0×10^{-8} to 4.0×10^{-7} can increase the reaction rate by a power of 10
- Small increases in $[H^+]$ can lead to **acidosis**; small decreases in $[H^+]$ can lead to **alkalosis**
- Effective control of many physiological reactions depends on pH control**

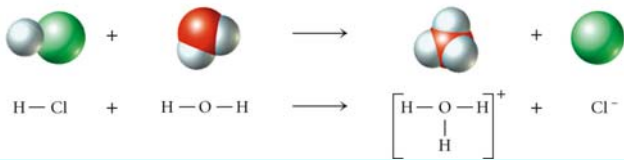
Example 13.2, (Cont'd)

ANALYSIS	
Information given:	pH (7.40)
Information implied:	K_w value
Asked for:	$[H^+]$ and $[OH^-]$
STRATEGY	
1. Substitute into Equation 13.3 to convert pH to $[H^+]$.	
2. Substitute into Equation 13.1 to obtain $[OH^-]$.	
SOLUTION	
1. $[H^+]$	$pH = -\log_{10}[H^+] \rightarrow 7.40 = -\log_{10}[H^+] \rightarrow [H^+] = 10^{-7.40} = 4.0 \times 10^{-8} M$
2. $[OH^-]$	$1.0 \times 10^{-14} = [OH^-](4.0 \times 10^{-8}) \rightarrow [OH^-] = 2.5 \times 10^{-7} M$

pH of Strong Acids

- Recall from Chapter 4 that some acids are strong
 - HCl, HBr, HI, $HClO_4$, HNO_3 , H_2SO_4
 - These completely ionize in water
 - $[H^+]$ is equal to the $[H^+]$ of the acid
- A 0.10 M solution of HCl has $[H^+] = 0.10 M$, so the pH of the solution is 1.00

Figure 13.3



Example 13.3, (Cont'd)

STUDENT B

ANALYSIS	
Information given:	pH (13.51) mass Ba(OH) ₂ added by Student A (4.23 g); volume of solution (455 mL)
Information implied:	molar mass of Ba(OH) ₂ ; K _w
Asked for:	mass Ba(OH) ₂ added compared with Student A continued

STRATEGY

- The pathway to follow is the reverse of that in part (a):
 $\text{pH} \xrightarrow{\text{Eq. 13.3}} [\text{H}^+] \xrightarrow{K_w} [\text{OH}^-] \xrightarrow{2[\text{OH}^-]/[\text{Ba}(\text{OH})_2]} [\text{Ba}(\text{OH})_2] \xrightarrow{V} \text{mol Ba}(\text{OH})_2 \xrightarrow{\text{MM}} \text{mass}$
- Compare masses used by Students A and B.

SOLUTION

[OH ⁻]	[H ⁺] = 10 ^{-13.51} = 3.1 × 10 ⁻¹⁴ M; [OH ⁻] = $\frac{1.0 \times 10^{-14}}{3.1 \times 10^{-14}}$ = 0.32 M
Mass Ba(OH) ₂ (Student B)	$\frac{0.32 \text{ mol OH}^-}{1 \text{ L}} \times \frac{1 \text{ mol Ba}(\text{OH})_2}{2 \text{ mol OH}^-} \times 0.455 \text{ L} \times \frac{171.3 \text{ g Ba}(\text{OH})_2}{1 \text{ mol}} = 12 \text{ g}$
Comparison	Student A: 4.32 g; Student B: 12 g 12 - 4.32 = 8 g more Ba(OH) ₂ were added by Student B.

pH of Strong Bases

- Recall as well that some bases are strong:
 - LiOH, NaOH, KOH, Ca(OH)₂, Sr(OH)₂, Ba(OH)₂
 - These bases ionize completely to OH⁻
 - pOH is dependent on the concentration of the strong base
- For an 0.10 M solution of NaOH,
 - [Na⁺] = [OH⁻] = 0.10 M
 - pOH = 1.00
 - pH = 13.00

Example 13.3, (Cont'd)

STUDENT C

ANALYSIS	
Information given:	from part (a); [OH ⁻] due to Ba(OH) ₂ (0.109 M); volume of solution (455 mL) mass of NaOH added (0.60 g)
Information implied:	molar mass of NaOH; K _w
Asked for:	pH of the solution

STRATEGY

- Find moles OH⁻ contributed by Ba(OH)₂ from part (a).
- Find moles OH⁻ contributed by NaOH.
- Find [OH⁻] after NaOH addition.

$$\frac{(\text{mol OH}^-)_{\text{Ba}(\text{OH})_2} + (\text{mol OH}^-)_{\text{NaOH}}}{V}$$
- Find [H⁺] and pH.

SOLUTION

1. mol OH ⁻ from Ba(OH) ₂	$\frac{0.109 \text{ mol OH}^-}{1 \text{ L}} \times 0.455 \text{ L} = 0.0496$
2. mol OH ⁻ from NaOH	$0.60 \text{ g NaOH} \times \frac{1 \text{ mol}}{40.0 \text{ g}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = 0.015$
3. [OH ⁻]	$\frac{0.0496 \text{ mol} + 0.015 \text{ mol}}{0.455 \text{ L}} = 0.14 \text{ M}$
4. [H ⁺] and pH	[H ⁺] = $\frac{1.0 \times 10^{-14}}{0.14} = 7.0 \times 10^{-14} \text{ M}$ pH = -log ₁₀ (7.0 × 10 ⁻¹⁴) = 13.15

Example 13.3

EXAMPLE 13.3 GRADED

Consider barium hydroxide, Ba(OH)₂, a white, powdery substance. Student A prepares a solution of Ba(OH)₂ by dissolving 4.23 g of Ba(OH)₂ in enough water to make 455 mL of solution.

- What is the pH of Student A's solution?
- Student B was asked to prepare the same solution as Student A. Student B's solution had a pH of 13.51. Did Student B add more or less Ba(OH)₂ to his solution? How much more or less Ba(OH)₂ was added?
- Student C was asked to add 0.60 g of NaOH to Student A's solution. What is the pH of Student C's solution? (Assume no volume change.)

STUDENT A

ANALYSIS	
Information given:	mass Ba(OH) ₂ (4.23 g); volume of solution (455 mL)
Information implied:	molar mass of Ba(OH) ₂ ; K _w
Asked for:	pH of the solution

STRATEGY

- Start by expressing the concentration in g Ba(OH)₂/L of solution.
- Follow the following pathway:

$$\text{mass Ba}(\text{OH})_2/\text{L} \xrightarrow{\text{MM}} [\text{Ba}(\text{OH})_2] \xrightarrow{2[\text{OH}^-]/[\text{Ba}(\text{OH})_2]} [\text{OH}^-] \xrightarrow{K_w} [\text{H}^+] \xrightarrow{\text{Eq. 13.3}} \text{pH}$$

SOLUTION

[OH ⁻]	$\frac{4.23 \text{ g Ba}(\text{OH})_2}{0.455 \text{ L}} \times \frac{1 \text{ mol Ba}(\text{OH})_2}{171.3 \text{ g}} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(\text{OH})_2} = 0.109 \text{ mol/L} = 0.109 \text{ M}$
[H ⁺]	$\frac{1.0 \times 10^{-14}}{0.109} = 9.2 \times 10^{-14} \text{ M}$
pH	pH = -log ₁₀ (9.2 × 10 ⁻¹⁴) = 13.04

Measuring pH

- pH can be measured with a pH meter
 - Translates [H⁺] into an electrical signal
 - Signal is shown on an analog or digital meter calibrated in pH units

Figure 13.4: pH of Carbonated Soda



Figure 13.6



pH Indicators

- Universal indicator
 - Mixture of substances that change color depending on the concentration of H^+
 - Less accurate than pH meter
 - Depending on the indicator used, can display pH over a narrow or wide range of $[H^+]$
- Some plants can act as pH indicators
 - Color of some flowers in plants is dependent on the pH of the soil in which the plant is grown

Weak Acids and their Equilibrium Constants

- Weak acids ionize only partially
- Prototype reaction
 - $HB(aq) + H_2O \rightleftharpoons H_3O^+(aq) + B^-(aq)$
- Two types of species that behave as weak acids
 1. Molecules with an ionizable hydrogen atom
 - $HNO_2(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NO_2^-(aq)$
 2. Cations
 - $NH_4^+(aq) + H_2O \rightleftharpoons H_3O^+(aq) + NH_3(aq)$

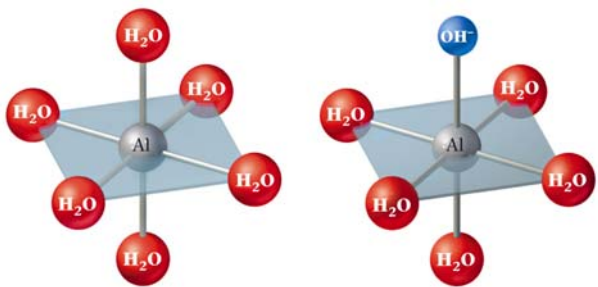
Figure 13.5: Universal Indicator



Metal Cations as Acids

- Many metal cations act as weak acids in water solution as well
 - $Zn(H_2O)_4^{2+}(aq) + H_2O \rightleftharpoons H_3O^+(aq) + Zn(H_2O)_3(OH)^+(aq)$
- The bond that forms between the oxygen and the metal ion weakens the O-H bond
- H^+ is more easily ionized as a result of the weakened bond

Figure 13.7



pK_a

- pK_a = -logK_a
- The smaller pK_a is, the stronger the acid
 - pK_a follows the trend for pH

Equilibrium Constants for Weak Acids

- HB (aq) + H₂O ⇌ H₃O⁺ (aq) + B⁻ (aq)
 - K_a is the acid equilibrium constant
 - Simplifying the above to HB (aq) ⇌ H⁺ (aq) + B⁻ (aq)

$$K_a = \frac{[H^+][B^-]}{[HB]}$$

- K_a values are related to the weak acid strength
 - The smaller K_a is, the weaker the acid is

Example 13.4

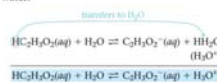
EXAMPLE 13.4

Consider acetic acid, HC₂H₃O₂, and the hydrated zinc cation, Zn(H₂O)₆²⁺.

- Write equations to show why these species are acidic.
- Which is the stronger acid?
- What is the pK_a of Zn(H₂O)₆²⁺?

STRATEGY AND SOLUTION

1. To prove that a species is acidic, you must produce a hydronium ion (H₃O⁺) obtained by transferring an H atom to water.



2. For the hydrated cation, one of the water molecules in the ion donates an H atom to an unattached water molecule. Think of Zn(H₂O)₆²⁺ as Zn(H₂O)(H₂O)₅²⁺.

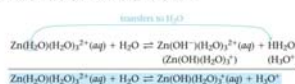


Table 13.2

Acid	K _a	Base	K _b	
Sulfuric acid	H ₂ SO ₄	1.7 × 10 ⁻²	HSO ₄ ⁻	5.9 × 10 ⁻⁸
Hydrogen sulfate ion	HSO ₄ ⁻	1.0 × 10 ⁻²	SO ₄ ²⁻	1.0 × 10 ⁻¹²
Phosphoric acid	H ₃ PO ₄	7.5 × 10 ⁻³	H ₂ PO ₄ ⁻	1.4 × 10 ⁻¹²
Hexaquaaluminum(III) ion	Fe(H ₂ O) ₆ ³⁺	6.7 × 10 ⁻²	Fe(H ₂ O) ₅ OH ²⁺	1.5 × 10 ⁻¹¹
Hydrofluoric acid	HF	6.9 × 10 ⁻⁴	F ⁻	1.4 × 10 ⁻¹¹
Nitrous acid	HNO ₂	6.0 × 10 ⁻⁴	NO ₂ ⁻	1.7 × 10 ⁻¹¹
Formic acid	HCO ₂ H	1.9 × 10 ⁻⁴	CO ₂ ⁻	5.3 × 10 ⁻¹¹
Lactic acid	HC ₃ H ₅ O ₂	1.4 × 10 ⁻⁴	C ₃ H ₅ O ₂ ⁻	7.1 × 10 ⁻¹¹
Benzoic acid	HC ₆ H ₅ CO ₂	6.6 × 10 ⁻⁵	C ₆ H ₅ CO ₂ ⁻	1.5 × 10 ⁻¹⁰
Acetic acid	HC ₂ H ₃ O ₂	1.8 × 10 ⁻⁵	C ₂ H ₃ O ₂ ⁻	5.6 × 10 ⁻¹⁰
Hexaquaaluminum(III) ion	Al(H ₂ O) ₆ ³⁺	1.2 × 10 ⁻⁵	Al(H ₂ O) ₅ OH ²⁺	8.3 × 10 ⁻¹⁰
Carbonic acid	H ₂ CO ₃	4.4 × 10 ⁻⁷	HCO ₃ ⁻	2.3 × 10 ⁻⁸
Dihydrogen phosphate ion	H ₂ PO ₄ ⁻	6.2 × 10 ⁻⁸	HPO ₄ ²⁻	1.6 × 10 ⁻⁷
Hydrogen sulfate ion	HSO ₄ ⁻	6.0 × 10 ⁻⁸	SO ₄ ²⁻	1.7 × 10 ⁻¹²
Hypochlorous acid	HOCl	2.8 × 10 ⁻⁸	OCl ⁻	3.6 × 10 ⁻⁷
Hydrocyanic acid	HCN	5.8 × 10 ⁻¹⁰	CN ⁻	1.7 × 10 ⁻⁵
Ammonium ion	NH ₄ ⁺	5.6 × 10 ⁻¹⁰	NH ₃	1.8 × 10 ⁻⁵
Tetraaquaaluminum(III) ion	Zn(H ₂ O) ₄ ²⁺	3.3 × 10 ⁻¹⁰	Zn(H ₂ O) ₃ OH ⁺	3.0 × 10 ⁻¹⁰
Hydrogen carbonate ion	HCO ₃ ⁻	4.7 × 10 ⁻¹¹	CO ₃ ²⁻	2.1 × 10 ⁻⁸
Hydrogen phosphate ion	HPO ₄ ²⁻	4.5 × 10 ⁻¹¹	PO ₄ ³⁻	2.2 × 10 ⁻¹²

$\text{HB}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{B}^-(\text{aq}) \quad K_a = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]}$
 $\text{B}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \rightleftharpoons \text{HB}(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_b = \frac{[\text{B}^-][\text{OH}^-]}{[\text{B}^-]}$

Example 13.4, (Cont'd)

b

SOLUTION

K_a values from Table 13.2

HC ₂ H ₃ O ₂ (K _a = 1.8 × 10 ⁻⁵)	vs	Zn(H ₂ O) ₆ ²⁺ (K _a = 3.3 × 10 ⁻¹⁰)
1.8 × 10 ⁻⁵	>	3.3 × 10 ⁻¹⁰

HC₂H₃O₂ is the stronger acid.

c

SOLUTION

pK_a

pK _a = -log ₁₀ K _a = -log ₁₀ (3.3 × 10 ⁻¹⁰) = 9.48
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Example 13.5

EXAMPLE 13.5

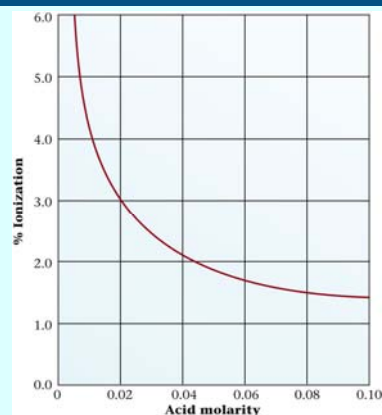
Aspirin, a commonly used pain reliever, is a weak organic acid whose molecular formula may be written as $\text{HC}_9\text{H}_7\text{O}_2$. An aqueous solution of aspirin has total volume 350.0 mL and contains 1.26 g of aspirin. The pH of the solution is found to be 2.60. Calculate K_a for aspirin.

ANALYSIS	
Information given:	molecular formula for aspirin ($\text{HC}_9\text{H}_7\text{O}_2$); mass of aspirin (1.26 g); volume of solution (350.0 mL); pH of solution (2.60)
Information implied:	molar mass of aspirin; $[\text{H}^+]$
Asked for:	K_a

STRATEGY

- Determine the original concentration, $[\text{HA}]_0$, of aspirin.
- $\text{pH} = [\text{H}^+]_{\text{eq}}$
- Draw a table as illustrated in Example 12.4. Substitute $[\text{HA}]_0$ for P_{A} , $\Delta[\text{H}^+]$ for ΔP , and $[\text{HA}]_{\text{eq}}$ for $P_{\text{A,eq}}$. Since only one H atom ionizes at a time, $\Delta[\text{H}^+]$ for all species is the same. Recall that $[\text{H}^+]$ stands for the concentration in molarity.
- Write the K expression for the ionization and calculate K_a .

Figure 13.8 - % Ionization and Concentration



Example 13.5, (Cont'd)

SOLUTION																									
1. $[\text{HA}]_0$ for aspirin	$\frac{1.26 \text{ g}}{0.3500 \text{ L}} \times \frac{1 \text{ mol}}{180.15 \text{ g}} = 0.0200 \text{ M}$																								
2. $[\text{H}^+]_{\text{eq}}$	$2.60 = -\log_{10}[\text{H}^+]; [\text{H}^+] = 10^{-2.60} = 2.5 \times 10^{-3} \text{ M}$																								
3. Table	<table border="1"> <thead> <tr> <th></th> <th>$\text{HC}_9\text{H}_7\text{O}_2(\text{aq})$</th> <th>$\rightleftharpoons$</th> <th>$\text{H}^+(\text{aq})$</th> <th>+</th> <th>$\text{C}_9\text{H}_7\text{O}_2^-(\text{aq})$</th> </tr> </thead> <tbody> <tr> <td>$[\text{H}^+]_0$</td> <td>0.0200</td> <td></td> <td>0.0000</td> <td></td> <td>0.0000</td> </tr> <tr> <td>$\Delta[\text{H}^+]$</td> <td>-0.0025</td> <td></td> <td>+0.0025</td> <td></td> <td>+0.0025</td> </tr> <tr> <td>$[\text{H}^+]_{\text{eq}}$</td> <td>0.0175</td> <td></td> <td>0.0025</td> <td></td> <td>0.0025</td> </tr> </tbody> </table>		$\text{HC}_9\text{H}_7\text{O}_2(\text{aq})$	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{C}_9\text{H}_7\text{O}_2^-(\text{aq})$	$[\text{H}^+]_0$	0.0200		0.0000		0.0000	$\Delta[\text{H}^+]$	-0.0025		+0.0025		+0.0025	$[\text{H}^+]_{\text{eq}}$	0.0175		0.0025		0.0025
	$\text{HC}_9\text{H}_7\text{O}_2(\text{aq})$	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{C}_9\text{H}_7\text{O}_2^-(\text{aq})$																				
$[\text{H}^+]_0$	0.0200		0.0000		0.0000																				
$\Delta[\text{H}^+]$	-0.0025		+0.0025		+0.0025																				
$[\text{H}^+]_{\text{eq}}$	0.0175		0.0025		0.0025																				
4. K expression	$\text{HC}_9\text{H}_7\text{O}_2(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{C}_9\text{H}_7\text{O}_2^-(\text{aq})$																								
K_a	$K_a = \frac{[\text{H}^+][\text{C}_9\text{H}_7\text{O}_2^-]}{[\text{HC}_9\text{H}_7\text{O}_2]} = \frac{(0.0025)(0.0025)}{0.0175} = 3.6 \times 10^{-4}$																								

END POINT

Aspirin is a relatively *strong* weak acid. It would be located near the top of Table 13.2.

Example 13.6

EXAMPLE 13.6 CONCEPTUAL

The box below shows a system at equilibrium. It has a volume of 0.50 L and the symbol \bullet represents 0.10 mol of a weak acid, HB. The symbol \circ represents 0.10 mol of the conjugate base, B^- . Hydronium ions and water molecules are not shown. What is the percent ionization of the acid?



STRATEGY

- Since there are 4 red circles (HB) and 1 blue circle (B^-) at equilibrium, there must have been 5 red circles to start with.
- Substitute into Equation 13.7.

$$\% \text{ ionization} = \frac{[\text{B}^-]_{\text{eq}}}{[\text{HB}]_0} \times 100$$

SOLUTION

% ionization	1 blue circle = $[\text{B}^-]_{\text{eq}}$; 5 red circles = $[\text{HB}]_0$
	$\% \text{ ionization} = \frac{1}{5} \times 100\% = 20\%$

Percent Ionization

- The percent ionization of a weak acid is defined as

$$\% \text{ ionization} = \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HB}]_{\text{initial}}} \times 100\%$$

- For the calculation in example 13.5, the percent ionization is about 12 %
 - Note that the percent ionization depends on the molarity of the weak acid

Calculating $[\text{H}^+]$ in a Water Solution of a Weak Acid

- We can use the process for calculating equilibrium pressure for gaseous reactions that we looked at in Chapter 12 to calculate the equilibrium concentration of $[\text{H}^+]$ for a weak acid
- The relationship between $[\text{HB}]$, $[\text{H}^+]$ and $[\text{B}^-]$ is given in the equilibrium expression itself

Example 13.7

EXAMPLE 13.7

Nicotinic acid, $\text{HC}_6\text{H}_4\text{O}_2\text{N}$ ($K_a = 1.4 \times 10^{-5}$), is another name for niacin, an important member of the vitamin B group. Determine $[\text{H}^+]$ in a solution prepared by dissolving 3.0 g of nicotinic acid (MM = 123.11 g/mol), HNic, in enough water to form 245 mL of solution.

ANALYSIS

Information given: molar mass for nicotinic acid, HNic (123.11 g/mol); mass of HNic (3.0 g)
volume of solution (245 mL)
 K_a (1.4×10^{-5})

Information implied: $[\text{HNic}]_0$

Asked for: $[\text{H}^+]_{\text{eq}}$

STRATEGY

- Determine the original concentration, $[\]_0$, of HNic.
- Let $x = \Delta[\text{H}^+]$.
Since all the coefficients in the reaction are one, $\Delta[\text{HNic}]$ and $\Delta[\text{Nic}^-]$ also equal x .
- Draw a table as illustrated in Example 13.5.
- Write the K_a expression for the ionization and substitute the equilibrium concentrations for HNic, Nic^- , and H^+ obtained from the table.
- Solve for x . (Assume $x \ll [\text{Nic}]_0$ to avoid the quadratic equation.)
- Substitute the value for x in $[\text{H}^+]_{\text{eq}}$.

Example 13.7, (Cont'd)

SOLUTION

1. $[\]_0$ for HNic

$$\frac{3.0 \text{ g}}{0.245 \text{ L}} \times \frac{1 \text{ mol}}{123.11 \text{ g}} = 0.10 \text{ M}$$

2. $\Delta[\]$

$$\Delta[\text{HNic}] = \Delta[\text{Nic}^-] = \Delta[\text{H}^+] = x$$

3. Table

	HNic(aq)	\rightleftharpoons	$\text{H}^+(\text{aq})$	+	$\text{Nic}^-(\text{aq})$
$[\]_0$	0.10		0.00		0.00
$\Delta[\]$	-x		+x		+x
$[\]_{\text{eq}}$	$0.10 - x$		x		x

4. K_a expression

$$1.4 \times 10^{-5} = \frac{[\text{H}^+][\text{Nic}^-]}{[\text{HNic}]} = \frac{(x)(x)}{0.10 - x}$$

5. Assume $x \ll 0.10$

$$1.4 \times 10^{-5} = \frac{(x)(x)}{0.10} \rightarrow x = 0.0012 \text{ M}$$

continued

Algebra Review – Quadratic Equations

- Recall that for a quadratic equation in the form

$$ax^2 + bx + c = 0$$

- The roots are

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

Approximations Used in Calculations

- The value of K_a is usually known no more accurately than about $\pm 5\%$

- When solving for the unknowns used to work the equilibrium problem, for the expression

$$K_a = \frac{x^2}{a - x}$$

- Where a is the initial concentration of weak acid, you can neglect x in the denominator if doing so does not introduce an error of more than 5%, i.e.,

$$\text{if } \frac{x}{a} \leq 0.05, \text{ then } a - x \approx a$$

Example 13.7, (Cont'd)

END POINT

Note that the concentration of H^+ , 0.0012 M, is

- much smaller than the original concentration of the weak acid, 0.10 M. In this case, then, the approximation $0.10 - x \approx 0.10$ is justified. This will usually, but not always, be the case (see Example 13.8).

- much larger than $[\text{H}^+]$ in pure water, $1 \times 10^{-7} \text{ M}$, justifying the assumption that the ionization of water can be neglected. This will always be the case, provided $[\text{H}^+]$ from the weak acid is $\geq 10^{-6} \text{ M}$.

Approximations and Percent Ionization

- When
$$\frac{x}{a} = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HB}]_0}$$

- Multiplying by 100% will give the percent ionization:

$$\frac{x}{a} \% = \frac{[\text{H}^+]_{\text{eq}}}{[\text{HB}]_0} \times 100\%$$

- If the percent ionization is 5% or less, you may make the approximation.
- If the percent ionization is greater than 5%, the quadratic formula or the successive approximation method is required

Example 13.8

EXAMPLE 13.8

Calculate $[H^*]$ in a 0.100 M solution of nitrous acid, HNO_2 , for which $K_a = 6.0 \times 10^{-4}$.

ANALYSIS

Information given:	$[HNO_2]_0$ (0.100 M); K_a (6.0×10^{-4})
Asked for:	$[H^*] = [H^*]_{eq}$ continued

Example 13.8, (Cont'd)

STRATEGY

1. The table setup is identical to that of Example 13.7 giving the equilibrium expression

$$K_a = \frac{[H^*][NO_2^-]}{[HNO_2]} = \frac{(x)(x)}{0.100 - x}$$

2. Assume $x \ll 0.100$ and solve for x .

3. Check your assumption by calculating % ionization.

If the % ionization is less than 5%, your assumption is valid. If not, solve for x using the quadratic equation.

Polyprotic Weak Acids

- Acids containing more than one ionizable hydrogen are called polyprotic
 - The anion formed in one step produces another H^+ in a successive ionization step
 - The equilibrium constant becomes smaller with each successive step

Triprotic Acid

- Phosphoric acid
 - $H_3PO_4(aq) \rightleftharpoons H^+(aq) + H_2PO_4^-(aq)$ K_{a1}
 - $H_2PO_4^-(aq) \rightleftharpoons H^+(aq) + HPO_4^{2-}(aq)$ K_{a2}
 - $HPO_4^{2-}(aq) \rightleftharpoons H^+(aq) + PO_4^{3-}(aq)$ K_{a3}
- $K_{a1} > K_{a2} > K_{a3}$
- With each successive step, **the acid becomes progressively weaker**

Example 13.8, (Cont'd)

SOLUTION

Equilibrium expression	$6.0 \times 10^{-4} = \frac{[H^*][NO_2^-]}{[HNO_2]} = \frac{(x)(x)}{0.100 - x}$
Assume $x \ll 0.100$.	$6.0 \times 10^{-4} = \frac{x^2}{0.100} \rightarrow x = 0.0077 M = [H^*]$
Check the assumption.	% ionization = $\frac{[H^*]_{eq}}{[HB]_0} \times 100\% = \frac{0.0077}{0.100} \times 100\% = 7.7\%$ $7.7\% > 5.0\% \rightarrow$ The assumption is not valid.
Use the quadratic equation.	$x^2 + (6.0 \times 10^{-4})x - (6.0 \times 10^{-5}) = 0$ $x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(6.0 \times 10^{-4}) \pm \sqrt{(6.0 \times 10^{-4})^2 - 4(6.0 \times 10^{-5})}}{2}$ $x = 0.0074 M$ or $-0.0080 M$ $-0.0080 M$ is physically impossible, so $x = [H^*] = 0.0074 M$

Table 13.3

TABLE 13.3 Equilibrium Constants for Some Weak Polyprotic Acids at 25°C

Acid	Formula	K_{a1}	K_{a2}	K_{a3}
Carbonic acid*	H_2CO_3	4.4×10^{-7}	4.7×10^{-11}	
Oxalic acid	$H_2C_2O_4$	5.9×10^{-2}	5.2×10^{-5}	
Phosphoric acid	H_3PO_4	7.1×10^{-3}	6.2×10^{-8}	4.5×10^{-13}
Sulfurous acid	H_2SO_3	1.7×10^{-2}	6.0×10^{-8}	

*Carbonic acid is a water solution of carbon dioxide:



Example 13.9

EXAMPLE 13.9

The distilled water you use in the laboratory is slightly acidic because of dissolved CO_2 , which reacts to form carbonic acid, H_2CO_3 . Calculate the pH of a 0.0010 M solution of H_2CO_3 and $[\text{CO}_3^{2-}]_{\text{eq}}$ at equilibrium.

ANALYSIS

Information given:	$[\text{H}_2\text{CO}_3]_0$ (0.0010 M)
Information implied:	two-step ionization, K_a value for each ionization (Table 13.3)
Asked for:	pH, $[\text{CO}_3^{2-}]_{\text{eq}}$

STRATEGY

- Write the ionization reactions and the K_a expression for each ionization. Recall that ionization of polyprotic acids takes place one H^+ at a time and that most of the H^+ is obtained from the first ionization.
- Find $[\text{H}^+]_{\text{eq}}$ for the first ionization and convert to pH.
- Note $[\text{H}^+] = [\text{HCO}_3^-]$. Substitute into the expression for the second ionization to obtain $[\text{CO}_3^{2-}]_{\text{eq}}$.

SOLUTION

First ionization	$\text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \quad K_{a1} = 4.4 \times 10^{-7}$ $4.4 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.0010 - x}$
Assume $x \ll 0.0010$.	$4.4 \times 10^{-7} = \frac{x^2}{0.0010} \rightarrow x^2 = (0.0010)(4.4 \times 10^{-7}) \rightarrow x = 2.1 \times 10^{-5} \text{ M}$
Check assumption.	% ionization = 2.1%; assumption is valid.
pH	$[\text{H}^+] = [\text{HCO}_3^-] = 2.1 \times 10^{-5} \text{ M}$; pH = 4.68 continued

Example 13.10

EXAMPLE 13.10

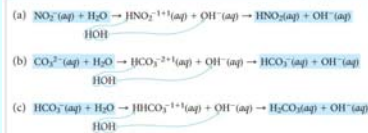
Write an equation to explain why each of the following produces a basic water solution.

- (a) NO_2^- (b) Na_2CO_3 (c) KHCO_3

STRATEGY

- React each basic anion with a water molecule.
- The weak base picks up the proton (H^+) and increases its charge by one unit to create its conjugate acid.
- OH^- is the other product of the reaction.

SOLUTION



END POINT

The presence of OH^- as a product is the reason these anions in water are considered to be basic.

Example 13.9, (Cont'd)

Second ionization	$\text{HCO}_3^-(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \quad K_{a2} = 4.7 \times 10^{-11}$ $4.7 \times 10^{-11} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$
$[\text{CO}_3^{2-}]$	From first ionization: $[\text{H}^+] = [\text{HCO}_3^-]$, so $K_{a2} = [\text{CO}_3^{2-}] = 4.7 \times 10^{-11} \text{ M}$

Weak Base Equilibrium Constant

- $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - The **base equilibrium constant, K_b** is

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

- For a generic weak base where
 - $\text{B}(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HB}^+(\text{aq}) + \text{OH}^-(\text{aq})$

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

Weak Bases and their Equilibrium Expressions

- Types of weak bases
 - Molecules
 - Ammonia, NH_3 , and amines
 - $\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$
 - Anions
 - Anions derived from weak acids are weak bases
 - $\text{I}^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HI}(\text{aq}) + \text{OH}^-(\text{aq})$

K_b by the Numbers

- As K_b becomes larger, base strength increases
- As with acids and K_a , we can define a $\text{p}K_b$:
 - $\text{p}K_b = -\log K_b$
 - As $\text{p}K_b$ becomes smaller, base strength increases

Calculation of [OH⁻] in a Weak Base Solution

- The process of calculating the [OH⁻] in a weak base solution is the same as the process for calculating [H⁺] in a weak acid solution

Example 13.11, (Cont'd)

3. K_b expression	$K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]} = 3.6 \times 10^{-7} = \frac{(x)(x)}{0.193-x}$
Assume $x \ll 0.193$	$x^2 = 0.193(3.6 \times 10^{-7}) \rightarrow x = 2.6 \times 10^{-4}$
Check assumption	% ionization = 0.14%; the assumption is justified. [OH ⁻] = 2.6×10^{-4} M
4. [H ⁺]; pH	$1.0 \times 10^{-14} = [\text{H}^+](2.6 \times 10^{-4}) \rightarrow [\text{H}^+] = 3.9 \times 10^{-11} \rightarrow \text{pH} = 10.41$

B

ANALYSIS

Information given:	NaOCl content of household bleach (5.25% by mass) density of bleach (1.00 g/mL) pH of solution in part (a) (10.41)
Asked for:	Compare pH of solution (a) and pH of bleach.

Example 13.11

EXAMPLE 13.11 GRADED

Consider sodium hypochlorite, NaOCl, the main component in household bleach. The hypochlorite ion, OCl⁻, has $K_b = 3.6 \times 10^{-7}$. A solution is prepared by dissolving 12.0 g of NaOCl (MM = 74.45 g/mol) in enough water to make 835 mL of solution.

- What is the pH of the solution?
- Household bleach is 5.25% NaOCl by mass. Assuming that its density is 1.00 g/mL, is household bleach more alkaline than the prepared solution?

a

ANALYSIS

Information given:	K_b for OCl ⁻ (3.6×10^{-7}) mass of NaOCl (12.0 g); molar mass of NaOCl (74.45 g/mol) volume of solution (0.835 L)
Information implied:	K_w
Asked for:	pH of the solution

Example 13.11, (Cont'd)

STRATEGY

- Assume 100.0 g (= 100.0 mL) of bleach. Thus, there are 5.25 g of NaOCl in 100.0 mL of solution.
- Find [OH⁻], [H⁺], and pH of bleach as in part (a).
- Compare the pH of both solutions. The solution with a higher pH is more alkaline.

SOLUTION

$[\text{NaOCl}]_0 = [\text{OCl}^-]_0$	$\frac{5.25 \text{ g}}{100.0 \text{ L}} \times \frac{1 \text{ mol}}{74.45 \text{ g}} = 0.705 \text{ M}$
K_b expression	(as in part (a)): $K_b = \frac{[\text{HOCl}][\text{OH}^-]}{[\text{OCl}^-]} = 3.6 \times 10^{-7} = \frac{(x)(x)}{0.705-x}$
Assume $x \ll 0.705$	$x^2 = 0.705(3.6 \times 10^{-7}) \rightarrow x = 5.0 \times 10^{-4}$
Check assumption.	% ionization = 0.071%; the assumption is justified. [OH ⁻] = 5.0×10^{-4} M
[H ⁺]; pH	$1.0 \times 10^{-14} = [\text{H}^+](5.0 \times 10^{-4}) \rightarrow [\text{H}^+] = 2.0 \times 10^{-11} \rightarrow \text{pH} = 10.70$
Comparison	pH of the solution in part (a) = 10.41; pH of bleach = 10.70 10.70 > 10.41; bleach is more alkaline than the solution prepared in part (a).

Example 13.11, (Cont'd)

STRATEGY

- Determine the original concentration, []₀, of NaOCl.
- Draw a table as illustrated in Example 13.5.
- Write the K_b expression and find [OH⁻] assuming [OH⁻]₀ << [OCl⁻]₀. Check the validity of the assumption by finding % ionization.
- Find [H⁺] using Equation 13.1 and pH using Equation 13.3.

SOLUTION

1. [] ₀ for NaOCl	$\frac{12.0 \text{ g}}{0.835 \text{ L}} \times \frac{1 \text{ mol}}{74.45 \text{ g}} = 0.193 \text{ M}$																								
2. Table	<table border="1"> <tr> <td></td> <td>OCl⁻(aq)</td> <td>+ H₂O</td> <td>⇌</td> <td>HOCl(aq)</td> <td>+ OH⁻(aq)</td> </tr> <tr> <td>[]₀</td> <td>0.193</td> <td></td> <td></td> <td>0.00</td> <td>0.00</td> </tr> <tr> <td>Δ[]</td> <td>-x</td> <td></td> <td></td> <td>+x</td> <td>+x</td> </tr> <tr> <td>[]_{eq}</td> <td>0.193 - x</td> <td></td> <td></td> <td>x</td> <td>x</td> </tr> </table>		OCl ⁻ (aq)	+ H ₂ O	⇌	HOCl(aq)	+ OH ⁻ (aq)	[] ₀	0.193			0.00	0.00	Δ[]	-x			+x	+x	[] _{eq}	0.193 - x			x	x
	OCl ⁻ (aq)	+ H ₂ O	⇌	HOCl(aq)	+ OH ⁻ (aq)																				
[] ₀	0.193			0.00	0.00																				
Δ[]	-x			+x	+x																				
[] _{eq}	0.193 - x			x	x																				

continued

Relation between K_a and K_b

- Consider the relation between a conjugate acid-base pair
 - $\text{HB}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{B}^-(\text{aq}) \quad K_f = K_a \text{ of HB}$
 - $\text{B}^-(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{HB}(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_{f2} = K_b \text{ of B}^-$
- These add to
 - $\text{H}_2\text{O} \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq}) \quad K_{f3} = K_w$
- Since $K_f K_{f2} = K_{f3}$, $K_a K_b = K_w = 1.0 \times 10^{-14}$
 - for a conjugate acid base pair only
 - In log form, $\text{p}K_a + \text{p}K_b = \text{p}K_w = 14.00$

Notes on Acid-Base Strength

- K_a and K_b are inversely related
 - The larger K_a is, the smaller K_b is
- Features
 - Brønsted-Lowry acids
 - Strong acids
 - Weak acids
 - Acids weaker than water (conjugates of strong bases)
 - Brønsted-Lowry bases
 - Strong bases
 - Weak bases
 - Bases weaker than water (conjugates of strong acids)

Acid-Base Properties of Solutions of Salts

- A salt is an ionic solid containing a cation other than H^+ and an anion other than OH^- or O^{2-}
- We can predict whether a salt will be acidic, basic or neutral by
 1. Deciding what effect the cation has on water
 - Is it acidic or is it neutral?
 2. Deciding what effect the anion has on water
 - Is it basic or is it neutral?
 3. Combining the two effects to decide the behavior of the salt in water

Table 13.4

TABLE 13.4 Relative Strengths of Brønsted-Lowry Acids and Bases

K_a	Conjugate Acid	Conjugate Base	K_b
Very large	$HClO_4$	ClO_4^-	Very small
Very large	HCl	Cl^-	Very small
Very large	HNO_3	NO_3^-	Very small
	H_3O^+	H_2O	
6.9×10^{-4}	HF	F^-	1.4×10^{-11}
1.8×10^{-5}	$HCl_2H_3O_2$	$C_2H_3O_2^-$	5.6×10^{-10}
1.2×10^{-5}	$Al(H_2O)_6^{3+}$	$Al(H_2O)_5(OH)^{2+}$	8.3×10^{-10}
4.4×10^{-7}	H_2CO_3	HCO_3^-	2.3×10^{-8}
2.8×10^{-8}	$HClO$	ClO^-	3.6×10^{-7}
5.6×10^{-10}	NH_4^+	NH_3	1.8×10^{-5}
4.7×10^{-11}	HCO_3^-	CO_3^{2-}	2.1×10^{-4}
	H_2O	OH^-	
Very small	C_2H_5OH	$C_2H_5O^-$	Very large
Very small	OH^-	O^{2-}	Very large
Very small	H_2	H^-	Very large

Cations

- Weak acid or spectator ion?
 - Most cations are acidic
 - These will change the pH by more than 0.5 pH units in a 0.1 M solution
 - Exceptions – these are spectators
 - Alkali metal cations
 - Heavier alkaline earth cations (Ca^{2+} , Sr^{2+} , Ba^{2+})

Hydride ion

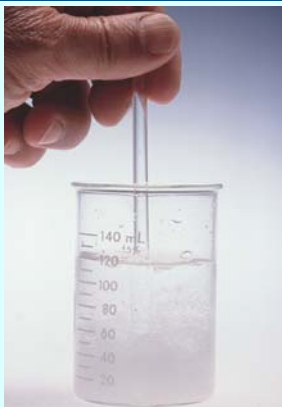
- Reaction of water with CaH_2
 - H^- is the conjugate base of H_2 , a very weak acid
 - As a result, H^- is an extremely strong base



Anions

- Weak base or spectator ion?
 - Many anions are weak bases
 - These will change the pH by more than 0.5 pH units at 0.1 M
 - Exceptions – these are spectators
 - Anions of very strong acids: Cl^- , Br^- , I^- , NO_3^- , ClO_4^-

Sodium Chloride Solution - Neutral



Amphiprotic Anions

- HCO_3^-
 - $K_a = 4.7 \times 10^{-11}$
 - $K_b = 2.3 \times 10^{-8}$
- Because $K_b > K_a$, a solution of NaHCO_3 will be basic

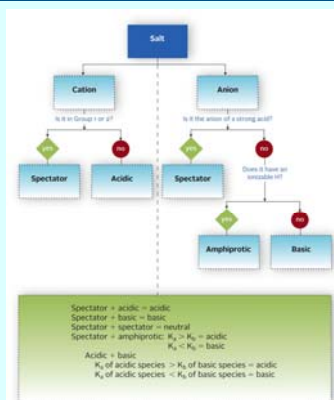
Table 13.5

TABLE 13.5 Acid-Base Properties of Ions* in Water Solution

	Spectator		Basic		Acidic	
Anion	Cl^- Br^- I^-	NO_3^- ClO_4^-	$\text{C}_2\text{H}_3\text{O}_2^-$ F^- Many others	CO_3^{2-} PO_4^{3-}		
Cation	Li^+ Na^+ K^+	Ca^{2+} Sr^{2+} Ba^{2+}			NH_4^+ Mg^{2+} Transition metal ions	Al^{3+}

*For the acid-base properties of amphiprotic anions such as HCO_3^- or H_2PO_4^- , see the discussion at the end of this section.

Figure 13.9: Flowchart for Acid-Base Properties of Salts



Salts: Acidic, Basic or Neutral

- By comparing the K_a of an acidic cation with the K_b of a basic anion, the salt of both can be classified as acidic, basic or neutral
 - If $K_a > K_b$, the salt is acidic
 - NH_4F , $K_a = 5.6 \times 10^{-10}$; $K_b = 1.4 \times 10^{-11}$
 - If $K_b > K_a$, the salt is basic
 - NH_4ClO , $K_a = 5.6 \times 10^{-10}$; $K_b = 3.6 \times 10^{-7}$

Example 13.12

EXAMPLE 13.12

Consider aqueous solutions of the following salts:

- (a) $\text{Zn}(\text{NO}_3)_2$ (b) KClO_4 (c) Na_2PO_4 (d) NH_4F (e) NaHCO_3

Which of these solutions are acidic? basic? neutral?

STRATEGY

Follow the flowchart in Figure 13.9.

Example 13.12, (Cont'd)

SOLUTION	
(a) cation: Zn^{2+}	not in group 1 or 2 \rightarrow acidic
anion: NO_3^-	anion of a strong acid \rightarrow spectator
$Zn(NO_3)_2$	acidic + spectator \rightarrow acidic
(b) cation: K^+	group 1 \rightarrow spectator
anion: ClO_4^-	anion of a strong acid \rightarrow spectator
$KClO_4$	spectator + spectator \rightarrow neutral
(c) cation: Na^+	group 1 \rightarrow spectator
anion: PO_4^{3-}	not an anion of a strong acid; no ionizable H \rightarrow basic
Na_3PO_4	spectator + basic \rightarrow basic
(d) cation: NH_4^+	not in group 1 or 2 \rightarrow acidic
anion: F^-	not an anion of a strong acid; no ionizable H \rightarrow basic
NH_4F	acidic + basic \rightarrow Check K_a for NH_4^+ and K_b for F^- K_a for $NH_4^+ = 5.6 \times 10^{-10}$; K_b for $F^- = 1.4 \times 10^{-11}$ $K_a > K_b \rightarrow NH_4F$ is acidic.
(e) cation: Na^+	group 1 \rightarrow spectator
anion: HCO_3^-	not an anion of a strong acid; has an ionizable H \rightarrow amphiprotic
$NaHCO_3$	spectator + amphiprotic \rightarrow Check K_a and K_b for HCO_3^- K_a for $HCO_3^- = 4.7 \times 10^{-11}$; K_b for $HCO_3^- = 2.3 \times 10^{-8}$ $K_b > K_a \rightarrow NaHCO_3$ is basic.

Lewis Acids

- The concept of a Lewis acid extends the acid-base model
 - The Lewis model greatly expands the number of species considered to be acids
 - For example, metal cations are *not* Brønsted-Lowry acids but are Lewis acids

Extending the Concept of Acids and Bases

- The Lewis Model
 - A Lewis base donates a pair of electrons
 - A Lewis acid accepts a pair of electrons

Table 13.6

TABLE 13.6 Alternative Definitions of Acids and Bases

Model	Acid	Base
Arrhenius	Supplies H^+ to water	Supplies OH^- to water
Brønsted-Lowry	H^+ donor	H^+ acceptor
Lewis	Electron pair acceptor	Electron pair donor

Lewis Bases

- The concept of a Lewis base does not structurally differ from that of a Brønsted-Lowry base
 - For a species to accept a proton, it must contain an atom that possesses a lone pair
 - Lewis bases are also Brønsted-Lowry bases

Key Concepts

- Classify a substance as a Brønsted-Lowry acid or base and write the net ionic equation to support the classification
- Given $[H^+]$, $[OH^-]$, pH or pOH, calculate the three other quantities
- Given the pH and original concentration of a weak acid, calculate K_a
- Given the K_a and original concentration of a weak acid, calculate $[H^+]$
- Given the K_b and original concentration of a weak base, calculate $[OH^-]$

Key Concepts, (Cont'd)



6. Given K_a for a weak acid, calculate K_b for its conjugate base (or vice-versa).
7. Predict whether a salt will be acidic, basic or neutral.
8. Understand the similarities and differences between Lewis and Brønsted-Lowry acids and bases