CHAPTER 14
THE CHEMISTRY OF ACIDS AND BASES

"ACID"--Latin word acidus, meaning sour. (lemon)
"ALKALI"--Arabic word for the ashes that come from burning certain plants; water solutions feel slippery and taste bitter. (soap)

Acids and bases are extremely important in many everyday applications: our own bloodstream, our environment, cleaning materials, industry. (sulfuric acid is an economic indicator!)

ACID-BASE THEORIES:

❖ ARRHENIUS DEFINITION
  - acid--donates a hydrogen ion (H⁺) in water
  - base--donates a hydroxide ion in water (OH⁻)

This theory was limited to substances with those "parts"; ammonia is a MAJOR exception!

❖ BRONSTED-LOWRY DEFINITION
  - acid--donates a proton in water
  - base--accepts a proton in water

This theory is better; it explains ammonia as a base! This is the main theory that we will use for our acid/base discussion.

❖ LEWIS DEFINITION
  - acid--accepts an electron pair
  - base--donates an electron pair

This theory explains all traditional acids and bases + a host of coordination compounds and is used widely in organic chemistry. Uses coordinate covalent bonds

THE BRONSTED-LOWRY CONCEPT OF ACIDS AND BASES
Using this theory, you should be able to write weak acid/base dissociation equations and identify acid, base, conjugate acid and conjugate base.

- conjugate acid-base pair--A pair of compounds that differ by the presence of one H⁺ unit. This idea is critical when it comes to understanding buffer systems. Pay close attention here!
- acids--donate a proton (H⁺)

\[
\begin{align*}
\text{acid} + \text{base} & \rightarrow \text{neutral compound} \\
\text{HNO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^- \\
\text{NH}_4^+ + \text{H}_2\text{O} & \rightarrow \text{H}_3\text{O}^+ + \text{NH}_3 \\
\end{align*}
\]
H$_2$PO$_4$ + H$_2$O $\rightleftharpoons$ H$_3$O$^+$ + HPO$_4^{2-}$  

**acid**  **base**  **CA**  **CB**  anion

In each of the acid examples---notice the formation of H$_3$O$^+$ -- this species is named the **hydronium ion**. It lets you know that the solution is **acidic**!

( *hydronium*, H$_3$O$^+$--H$^+$ riding piggy-back on a water molecule; water is polar and the + charge of the naked proton is greatly attracted to Mickey's chin!)

- **bases**--accept a proton (H$^+$)

NH$_3$ + H$_2$O $\rightleftharpoons$ NH$_4^+$ + OH$^-$  

**base**  **acid**  **CA**  **CB**  neutral compound

CO$_3^{2-}$ + H$_2$O $\rightleftharpoons$ HCO$_3^-$ + OH$^-$  

**base**  **acid**  **CA**  **CB**  anion

PO$_4^{3-}$ + H$_2$O $\rightleftharpoons$ HPO$_4^{2-}$ + OH$^-$  

**base**  **acid**  **CA**  **CB**  anion

In each of the basic examples---notice the formation of OH$^-$ -- this species is named the **hydroxide ion**. It lets you know that the solution is **basic**!

**You try!!**

**Exercise 1**

a) In the following reaction, identify the acid on the left and its CB on the right. Similarly identify the base on the left and its CA on the right.

HBr + NH$_3$ $\rightarrow$ NH$_4^+$ + Br$^-$

b) What is the conjugate base of H$_2$S?

c) What is the conjugate acid of NO$_3^-$?
ACIDS ONLY DONATE ONE PROTON AT A TIME!!!

- **monoprotic**—acids donating one H⁺ (ex. HCl₂H₃O₂)
- **diprotic**—acids donating two H⁺’s (ex. H₂C₂O₄)
- **polyprotic**—acids donating many H⁺’s (ex. H₃PO₄)

- **polyprotic bases**—accept more than one H⁺; anions with -2 and -3 charges (ex. PO₄³⁻; HPO₄²⁻)

- **Amphiprotic or amphoteric**—molecules or ions that can behave as EITHER acids or bases; water, anions of weak acids (look at the examples above—sometimes water was an acid, sometimes it acted as a base)

**Exercise 2  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 (HC₂H₃O₂)

c. The ammonium ion (NH₄⁺)

d. The anilinium ion (C₆H₅NH₃⁺)

e. The hydrated aluminum(III) ion [Al(H₂O)₆]³⁺

<table>
<thead>
<tr>
<th></th>
<th>Before dissociation</th>
<th>After dissociation, at equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HCl(aq)</td>
<td>H⁺(aq) + Cl⁻(aq)</td>
</tr>
<tr>
<td>B</td>
<td>HC₂H₃O₂(aq)</td>
<td>H⁺(aq) + C₂H₂O₂⁻(aq)</td>
</tr>
<tr>
<td>C</td>
<td>NH₄⁺(aq)</td>
<td>H⁺(aq) + NH₃(aq)</td>
</tr>
<tr>
<td>D</td>
<td>C₆H₅NH₃⁺(aq)</td>
<td>H⁺(aq) + C₆H₅NH₂(aq)</td>
</tr>
<tr>
<td>E</td>
<td>Al(H₂O)₆³⁺(aq)</td>
<td>H⁺(aq) + Al(H₂O)₃OH²⁺(aq)</td>
</tr>
</tbody>
</table>

**RELATIVE STRENGTHS OF ACIDS AND**

Rene McCormick & Lisa McGaw
Advanced Placement Strategies, Inc.
BASES
Strength is determined by the position of the "dissociation" equilibrium.

- **Strong** acids/strong bases -
  1. dissociates completely in water
  2. have very large K values

- **Weak** acids/weak bases -
  1. dissociate only to a slight extent in water
  2. dissociation constant is very small

Do Not confuse concentration with strength!

- **STRONG ACIDS:**
  - Hydrohalic acids: HCl, HBr, HI
  - Nitric: HNO₃
  - Sulfuric: H₂SO₄
  - Perchloric: HClO₄

The *more oxygen* present in the polyatomic ion, the *stronger* its acid *WITHIN* that group.

- **STRONG BASES:**
- Hydroxides OR oxides of IA and IIA metals
  - Solubility plays a role (those that are very soluble are strong!)

**THE STRONGER THE ACID THE WEAKER ITS CB, the converse is also true.**

<table>
<thead>
<tr>
<th>Relative acid strength</th>
<th>Relative conjugate base strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very strong</td>
<td>Very strong</td>
</tr>
<tr>
<td>Strong</td>
<td>Very weak</td>
</tr>
<tr>
<td>Weak</td>
<td>Weak</td>
</tr>
<tr>
<td>Very weak</td>
<td>Strong</td>
</tr>
</tbody>
</table>

**WEAK ACIDS AND BASES: Equilibrium expressions**

- The vast majority of acid/bases are weak. Remember, this means they do not ionize much.

The equilibrium expression for acids is known as the $K_a$ (the acid dissociation constant). It is set up the same way as in general equilibrium. Many common weak acids are oxyacids, like phosphoric acid and nitrous acid. Other common weak acids are organic acids—those that contain a carboxyl group—COOH group, like acetic acid and benzoic acid.

For weak acid reactions: $\text{HA} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{A}^-$

**Table 14.1 Various Ways to Describe Acid Strength**

<table>
<thead>
<tr>
<th>Property</th>
<th>Strong Acid</th>
<th>Weak Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_a$ value</td>
<td>$K_a$ is large</td>
<td>$K_a$ is small</td>
</tr>
<tr>
<td>Position of the dissociation (ionization) equilibrium</td>
<td>Far to the right</td>
<td>Far to the left</td>
</tr>
<tr>
<td>Equilibrium concentration of $\text{H}^+$ compared with original concentration of HA</td>
<td>$[\text{H}^+] \approx [\text{HA}]_0$</td>
<td>$[\text{H}^+] \ll [\text{HA}]_0$</td>
</tr>
<tr>
<td>Strength of conjugate base compared with that of water</td>
<td>$\text{A}^-$ much weaker</td>
<td>$\text{A}^-$ much stronger</td>
</tr>
</tbody>
</table>

**Table 14.2 Values of $K_a$ for Some Common Monoprotic Acids**

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Value of $K_a$</th>
<th>$[\text{H}_3\text{O}^+][\text{A}^-]/[\text{HA}]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_{2}\text{SO}_4$</td>
<td>Hydrogen sulfate ion</td>
<td>$1.2 \times 10^{-2}$</td>
<td>Increasing acid strength</td>
</tr>
<tr>
<td>$\text{HClO}_2$</td>
<td>Chlorous acid</td>
<td>$1.2 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$\text{HClO}_3$</td>
<td>Chloric acid</td>
<td>$1.2 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>$\text{HBrO}_2$</td>
<td>Monochloroacetic acid</td>
<td>$1.35 \times 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td>$\text{HBrO}_3$</td>
<td>Hydrobromic acid</td>
<td>$7.2 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>$\text{HNO}_2$</td>
<td>Nitrous acid</td>
<td>$4.0 \times 10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>$\text{HNO}_3$</td>
<td>Acetic acid</td>
<td>$1.8 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_{2}\text{C}_2\text{H}_3\text{O}_2$</td>
<td>Hydroxide of acetic acid</td>
<td>$1.4 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>$\text{H}_{2}\text{C}_2\text{H}_2\text{O}_3$</td>
<td>Hydroxyacetic acid</td>
<td>$3.5 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>$\text{HCN}$</td>
<td>Hydrocyanic acid</td>
<td>$6.2 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>$\text{NH}_4^+$</td>
<td>Ammonium ion</td>
<td>$5.6 \times 10^{-10}$</td>
<td></td>
</tr>
<tr>
<td>$\text{HOCl}$</td>
<td>Hypochlorous acid</td>
<td>$1.6 \times 10^{-10}$</td>
<td></td>
</tr>
</tbody>
</table>

$^*$The units of $K_a$ are customarily omitted.
♦ Write the $K_a$ expression for acetic acid using Bronsted-Lowry. (Note: Water is a pure liquid and is thus, left out of the equilibrium expression.)

♦ Weak bases (bases without $\text{OH}^-$) react with water to produce a hydroxide ion. Common examples of weak bases are ammonia ($\text{NH}_3$), methylamine ($\text{CH}_3\text{NH}_2$), and ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$). The lone pair on N forms a bond with a $\text{H}^+$. Most weak bases involve N.

![Diagram of amine structures]

The equilibrium expression for bases is known as the $K_b$.

for weak base reactions: \[ \text{B} + \text{H}_2\text{O} \rightarrow \text{HB}^+ + \text{OH}^- \]

| Table 14.3 Values of $K_b$ for Some Common Weak Bases |
| --- | --- | --- | --- |
| Name | Formula | Conjugate Acid | $K_b$ |
| Ammonia | $\text{NH}_3$ | $\text{NH}_4^+$ | $1.8 \times 10^{-5}$ |
| Methylamine | $\text{CH}_3\text{NH}_2$ | $\text{CH}_3\text{NH}_3^+$ | $4.38 \times 10^{-4}$ |
| Ethylamine | $\text{C}_2\text{H}_5\text{NH}_2$ | $\text{C}_2\text{H}_5\text{NH}_3^+$ | $5.6 \times 10^{-4}$ |
| Aniline | $\text{C}_6\text{H}_5\text{NH}_2$ | $\text{C}_6\text{H}_5\text{NH}_3^+$ | $3.8 \times 10^{-10}$ |
| Pyridine | $\text{C}_5\text{H}_5\text{N}$ | $\text{C}_5\text{H}_5\text{NH}_3^+$ | $1.7 \times 10^{-9}$ |

$K_b = \frac{[\text{H}_2\text{O}^+][\text{OH}^-]}{[\text{B}] < 1}$
Set up the $K_b$ expression for ammonia using Bronsted-Lowry.

Notice that $K_a$ and $K_b$ expressions look very similar. The difference is that a base produces the hydroxide ion in solution, while the acid produces the hydronium ion in solution.

Another note on this point: $H^+$ and $H_3O^+$ are both equivalent terms here. Often water is left completely out of the equation since it does not appear in the equilibrium. This has become an accepted practice. (*However, water is very important in causing the acid to dissociate.)*

**Exercise 3**

**Relative Base Strength**

Using table 14.2, arrange the following species according to their strength as bases:

$H_2O$, $F^-$, $Cl^-$, $NO_2^-$, and $CN^-$.  

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

**WATER, THE HYDRONIUM ION, AUTO-IONIZATION, AND THE pH SCALE**

Fredrich Kohlrausch, around 1900, found that no matter how pure water is, it still conducts a minute amount of electric current. This proves that water self-ionizes.

Since the water molecule is amphoteric, it may dissociate with itself to a slight extent.

Only about 2 out of a billion water molecules are ionized at any instant!

\[
H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}
\]
The equilibrium expression used here is referred to as the $K_w$ (ionization constant for water).

In pure water or dilute aqueous solutions, the concentration of water can be considered to be a constant (55.4 M), so we include that with the equilibrium constant and write the expression as:

$$K_{eq}[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

$$K_w = 1.0 \times 10^{-14} \ (K_w = 1.008 \times 10^{-14} @ 25 \ degrees \ Celsius)$$

Knowing this value allows us to calculate the $[OH^-]$ and $[H^+]$ concentration for various situations.

- $[OH^-] = [H^+]$ solution is neutral (in pure water, each of these is $1.0 \times 10^{-7}$)
- $[OH^-] > [H^+]$ solution is basic
- $[OH^-] < [H^+]$ solution is acidic
- $K_w = K_a \times K_b$ (another very beneficial equation)

Exercise 5

Autoionization of Water

At 60°C, the value of $K_w$ is $1 \times 10^{-13}$.

a. Using Le Chatelier’s principle, predict whether the reaction

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

is exothermic or endothermic.

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

A: endothermic

B: $[H^+] = [OH^-] = 3 \times 10^{-7} \ M$

The pH Scale

- Used to designate the $[H^+]$ in most aqueous solutions
where \( H^+ \) is small.

- \( pH = - \log [H^+] \)
- \( pOH = - \log [OH^-] \)
- \( pH + pOH = 14 \)
- \( pH = 6.9 \) and lower (acidic)
  - \( = 7.0 \) (neutral)
  - \( = 7.1 > \) (basic)

* Use as many decimal places as there are sig.figs. in the problem!
  - The negative base 10 logarithm of the hydronium ion concentration becomes the whole number; therefore, only the decimals to the right are significant.

### Exercise 6  Calculating [H+] and [OH-]

Calculate [H+] or [OH-] as required for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

a. \( 1.0 \times 10^{-5} \text{ M} \text{OH}^- \)

b. \( 1.0 \times 10^{-7} \text{ M} \text{OH}^- \)

c. \( 10.0 \text{ M} H^+ \)

A: \( [H^+] = 1.0 \times 10^{-9} \text{ M} \), basic
B: \( [H^+] = 1.0 \times 10^{-7} \text{ M} \), neutral
C: \( [OH^-] = 1.0 \times 10^{-15} \text{ M} \), acidic

### Exercise 7  Calculating pH and pOH

Calculate pH and pOH for each of the following solutions at 25°C.

a. \( 1.0 \times 10^{-3} \text{ M} \text{OH}^- \)
b. $1.0 \, M \, H^+$

<table>
<thead>
<tr>
<th>pH</th>
<th>pOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: 11.00</td>
<td>3.00</td>
</tr>
<tr>
<td>B: 0.00</td>
<td>14.00</td>
</tr>
</tbody>
</table>

### Exercise 8  Calculating 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.

\[
pOH = 6.59
\]
\[
[H^+] = 3.9 \times 10^{-8}
\]
\[
[OH^-] = 2.6 \times 10^{-7} \, M
\]

### Exercise 9  pH of Strong Acids

a. Calculate the pH of 0.10 $M$ HNO$_3$.

b. Calculate the pH of $1.0 \times 10^{-10} \, M$ HCl.

A: pH = 1.00
B: pH = 7.00

### Exercise 10  The pH of Strong Bases

Calculate the pH of a $5.0 \times 10^{-2} \, M$ NaOH solution.
Calculating pH of Weak Acid Solutions

Calculating pH of weak acids involves setting up an equilibrium. Always start by writing the equation, setting up the acid equilibrium expression \( (K_a) \), defining initial concentrations, changes, and final concentrations in terms of \( x \), substituting values and variables into the \( K_a \) expression and solving for \( x \). (use the RICE diagram learned in general equilibrium!)

Ex. Calculate the pH of a \( 1.00 \times 10^{-4} \) M solution of acetic acid. The \( K_a \) of acetic acid is \( 1.8 \times 10^{-5} \)

\[
\text{HC}_2\text{H}_3\text{O}_2 \leftrightarrow \text{H}^+ + \text{C}_2\text{H}_3\text{O}_2^- \quad K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}
\]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC(\text{C}_2\text{H}_3\text{O}_2 )</td>
<td>(1.00 \times 10^{-4})</td>
<td>0</td>
<td>(1.00 \times 10^{-4} - x)</td>
</tr>
<tr>
<td>(\text{H}^+) + C(\text{C}_2\text{H}_3\text{O}_2^-)</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
1.8 \times 10^{-5} = \frac{(x)(x)}{1.00 \times 10^{-4} - x}
\]

Often, the \(-x\) in a \( K_a \) expression can be treated as negligible.

\[
1.8 \times 10^{-5} \approx \frac{(x)(x)}{1.00 \times 10^{-4}}
\]

\[
x = 4.2 \times 10^{-5}
\]

When you assume that \( x \) is negligible, you must check the validity of this assumption. To be valid, \( x \) must be less than 5% of the number that it was to be subtracted from. In this example \( 4.2 \times 10^{-5} \) is greater than 5% of \( 1.00 \times 10^{-4} \). This means that the assumption that \( x \) was negligible was invalid and \( x \) must be solved for using the quadratic equation or the method of successive approximation.

\[
\% \text{dissociation} = \frac{"x"}{[\text{original}]} \times 100
\]

\[
-b \pm \sqrt{b^2 - 4ac}
\]

Use of the quadratic equation: \( x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \)

\[
x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-9} = 0
\]
\[ -1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-1.8 \times 10^{-9})} \]

\[ x = \frac{-(-1.8 \times 10^{-5}) + \sqrt{(1.8 \times 10^{-5})^2 - 4(1)(-1.8 \times 10^{-9})}}{2(1)} \]

\[ x = 3.5 \times 10^{-5} \text{ and } -5.2 \times 10^{-5} \]

Since a concentration cannot be negative, \[ x = 3.5 \times 10^{-5} \text{ M} \]

\[ x = [H^+] = 3.5 \times 10^{-5} \quad \text{pH} = -\log 3.5 \times 10^{-5} = 4.46 \]

Another method which some people prefer is the method of successive approximations. In this method, you start out assuming that \( x \) is negligible, solve for \( x \), and repeatedly plug your value of \( x \) into the equation again until you get the same value of \( x \) two successive times.

---

**Exercise 11**

**The pH of Weak Acids**

The hypochlorite ion (\( \text{OCl}^- \)) 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\textsuperscript{-}, for example) and forms the weakly acidic hypochlorous acid (HOCl, $K_a = 3.5 \times 10^{-8}$). Calculate the pH of a 0.100 $M$ aqueous solution of hypochlorous acid.

\[ \text{pH} = 4.23 \]

\section*{Determination of the pH of a Mixture of Weak Acids}

- Only the acid with the largest $K_a$ value will contribute an appreciable $[H^+]$. Determine the pH based on this acid and ignore any others.

\section*{Exercise 12  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\textsubscript{2}($K_a = 4.0 \times 10^{-4}$). Also calculate the concentration of cyanide ion (CN\textsuperscript{-}) in this solution at equilibrium.

\[ \text{pH} = 1.35 \]
\[ [\text{CN}^-] = 1.4 \times 10^{-8} \ M \]

\section*{Exercise 13  Calculating Percent Dissociation}

Calculate the percent dissociation of acetic acid ($K_a = 1.8 \times 10^{-5}$) in each of the following solutions.
Exercise 14  Calculating $K_a$ from Percent Dissociation

Lactic acid ($\text{HC}_3\text{H}_5\text{O}_3$) is a waste product that accumulates in muscle tissue during exertion, leading to pain and a feeling of fatigue. In a 0.100 $M$ aqueous solution, lactic acid is 3.7% dissociated. Calculate the value of $K_a$ for this acid.

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

- Determination of the pH of a weak base is very similar to the determination of the pH of a weak acid. Follow the same steps. Remember, however, that $x$ is the $[\text{OH}^-]$ and taking the negative log of $x$ will give you the pOH and not the pH!
Calculate the pH for a 15.0 \( M \) solution of \( \text{NH}_3 \) (\( K_b = 1.8 \times 10^{-5} \)).

\[
\text{pH} = 12.20
\]

**Exercise 16**  
**The pH of Weak Bases II**

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

\[
\text{pH} = 12.32
\]

**Calculating pH of polyprotic acids**

- Acids with more than one ionizable hydrogen will ionize in steps. Each dissociation has its own \( K_a \) value.
- The first dissociation will be the greatest and subsequent dissociations will have much smaller equilibrium constants. As each H is removed, the remaining acid gets weaker and therefore has a smaller \( K_a \). As the negative charge on the acid increases it becomes more difficult to remove the positively charged proton.

- Example: Consider the dissociation of phosphoric acid.
Looking at the $K_a$ values, it is obvious that only the first dissociation will be important in determining the pH of the solution.

- Except for $H_2SO_4$, polyprotic acids have $K_{a2}$ and $K_{a3}$ values so much weaker than their $K_{a1}$ value that the 2nd and 3rd (if applicable) dissociation can be ignored. The $[H^+]$ obtained from this 2nd and 3rd dissociation is negligible compared to the $[H^+]$ from the 1st dissociation. Because $H_2SO_4$ is a strong acid in its first dissociation and a weak acid in its second, we need to consider both if the concentration is more dilute than 1.0 M. The quadratic equation is needed to work this type of problem.

### Exercise 17
**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 $PO_4^{3-}$.

- $pH = 0.72$
- $[H_3PO_4] = 4.8 \ M$
- $[H_2PO_4^-] = 0.19 \ M$
- $[HPO_4^{2-}] = 6.2 \times 10^{-8} \ M$
- $[PO_4^{3-}] = 1.6 \times 10^{-19} \ M$

### Exercise 18
**The pH of a Sulfuric Acid**

Calculate the pH of a 1.0 $M$ $H_2SO_4$ solution.
Exercise 19  The pH of a Sulfuric Acid

Calculate the pH of a 1.0 X 10^-2 M H_2SO_4 solution.

\[ \text{pH} = 1.84 \]

\[ \text{pH} = 0.00 \]

**ACID-BASE PROPERTIES OF SALTS: HYDROLYSIS**

Salts are produced from the reaction of an acid and a base. (neutralization)

Salts are not always neutral. Some hydrolyze with water to produce acidic and basic solutions.

- **Neutral Salts**- Salts that are formed from the cation of a strong base and the anion of a strong acid form neutral solutions when dissolved in water. A salt such as NaNO_3 gives a neutral solution.

- **Basic Salts**- Salts that are formed from the cation of a strong base and the anion of a weak acid form basic solutions when dissolved in water. The anion hydrolyzes the water molecule to produce hydroxide ions and thus a basic solution. K_2S should be basic since S^{2-} is the CB of the very weak acid HS^- while K^+ does not hydrolyze appreciably.

\[
\text{S}^{2-} + \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{HS}^-
\]

strong base weak acid

- **Acid Salts**- Salts that are formed from the cation of a weak base and the anion of a strong acid form acidic solutions when dissolved in water. The cation hydrolyzes the water molecule to produce hydronium ions and thus an acidic solution. NH_4Cl should be weakly acidic, since NH_4^+ hydrolyzes to give an acidic solution, while Cl^- does not.
If both the cation and the anion contribute to the pH situation, compare $K_a$ to $K_b$.

- If $K_b$ is larger, basic! The converse is also true.

- The following will help predict acidic, basic, or neutral---however, you must explain using appropriate equations as proof!!!
  1. Strong acid + strong base = neutral salt
  2. Strong acid + weak base = acidic salt
  3. Weak acid + strong base = basic salt
  4. Weak acid + weak base = ? (must look at $K$ values to decide)

**Exercise 20**  
**The Acid-Base Properties of Salts**

Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral. Prove with appropriate equations.

- **a.** $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$
- **b.** $\text{NH}_4\text{CN}$
- **c.** $\text{Al}_2(\text{SO}_4)_3$

<table>
<thead>
<tr>
<th>A: neutral</th>
<th>B: basic</th>
<th>C: acidic</th>
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**Exercise 21**  
**Salts as Weak Bases**

Calculate the pH of a $0.30 \, M$ NaF solution. The $K_a$ value for HF is $7.2 \times 10^{-4}$.
Exercise 22  Salts as Weak Acids I

Calculate the pH of a 0.10 \( M \) \( \text{NH}_4\text{Cl} \) solution. The \( K_b \) value for \( \text{NH}_3 \) is \( 1.8 \times 10^{-5} \).

\[ pH = 8.31 \]

Exercise 23  Salts as Weak Acids II

Calculate the pH of a 0.010 \( M \) \( \text{AlCl}_3 \) solution. The \( K_a \) value for \( \text{Al(H}_2\text{O})_6^{3+} \) is \( 1.4 \times 10^{-5} \).

\[ pH = 5.13 \]

\[ pH = 3.43 \]

**THE LEWIS CONCEPT OF ACIDS AND BASES**

- **acid**--can accept a pair of electrons to form a coordinate covalent bond
- **base**--can donate a pair of electrons to form a coordinate covalent bond
Yes, this is the dot guy and the structures guy--he was extremely busy making your life difficult!

BF$_3$--most famous of all!!

**Exercise 24**
Tell whether each of the following is a Lewis acid or base: Draw structures as proof.

a) PH$_3$

b) BCl$_3$

c) H$_2$S

d) SF$_4$

**Exercise 25**
Lewis Acids and Basis

For each reaction, identify the Lewis acid and base.

a. Ni$^{2+}$(aq) + 6NH$_3$(aq) → Ni(NH$_3$)$_6^{2+}$(aq)
b. \( \text{H}^+(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) \)

A: Lewis acid = nickel(II) ion  
    Lewis base = ammonia
B: Lewis acid = proton  
    Lewis base = water molecule