"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, and 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 plus 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 now and it will pay off later!

  \[
  \text{HNO}_3 + \text{H}_2 \rightarrow \text{H}_3\text{O}^+ + \text{NO}_3^- \\
  \text{acid} \quad \text{base} \quad \text{CA} \quad \text{CB} \\
  \text{neutral compound as an acid} \\
  \]

  \[
  \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3 \\
  \text{acid} \quad \text{base} \quad \text{CA} \quad \text{CB} \\
  \text{cation as an acid} \\
  \]

  \[
  \text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-} \\
  \text{acid} \quad \text{base} \quad \text{CA} \quad \text{CB} \\
  \text{anion as an acid} \\
  \]

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

( *hydronium*, $\text{H}_3\text{O}^+$--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!)

$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  
neutral compound

<table>
<thead>
<tr>
<th>base</th>
<th>acid</th>
<th>CA</th>
<th>CB</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_3^{2-}$ + H$_2$O $\rightleftharpoons$ HCO$_3^-$ + OH$^-$</td>
<td>anion</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PO$_4^{3-}$ + H$_2$O $\rightleftharpoons$ HPO$_4^{2-}$ + OH$^-$</td>
<td>anion</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Notice the formation of $\text{OH}^-$ in each of the alkaline examples. This species is named the **hydroxide ion**. It lets you know that the resulting 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 DONATE ONLY ONE PROTON AT A TIME!!!**

- **monoprotic**--acids donating one H$^+$ (ex. HC$_2$H$_5$O$_2$)
- **diprotic**--acids donating two H$^+$s (ex. H$_2$C$_2$O$_4$)
- **polyprotic**--acids donating many H$^+$s (ex. H$_3$PO$_4$)

- **polyprotic bases**--accept more than one H$^+$; anions with $-2$ and $-3$ charges (ex. PO$_4^{3-}$; HPO$_4^{2-}$)
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⁺

A: HCl(aq) ⇌ H⁺(aq) + Cl⁻(aq)
B: HC₂H₃O₂(aq) ⇌ H⁺(aq) + C₂H₃O₂⁻(aq)
C: NH₄⁺(aq) ⇌ H⁺(aq) + NH₃(aq)
D: C₆H₅NH₃⁺(aq) ⇌ H⁺(aq) + C₆H₅NH₂(aq)
E: Al(H₂O)₆³⁺(aq) ⇌ H⁺(aq) + [Al(H₂O)₅OH]²⁺(aq)
RELATIVE STRENGTHS OF ACIDS AND BASES
Strength is determined by the position of the "dissociation" equilibrium.

- **Strong** acids/strong bases
  1. dissociates completely in water
  2. have very large dissociation or $K$ 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: Memorize these SIX
- Hydrohalic acids: HCl, HBr, HI—note HF is missing!
- Nitric: HNO₃
- Sulfuric: H₂SO₄
- Perchloric: HClO₄

---

**Table 14.7 Bond Strengths and Acid Strengths for Hydrogen Halides**

<table>
<thead>
<tr>
<th>Bond</th>
<th>Bond Strength (kJ/mol)</th>
<th>Acid Strength in Water</th>
</tr>
</thead>
<tbody>
<tr>
<td>H—F</td>
<td>565</td>
<td>Weak</td>
</tr>
<tr>
<td>H—Cl</td>
<td>427</td>
<td>Strong</td>
</tr>
<tr>
<td>H—Br</td>
<td>363</td>
<td>Strong</td>
</tr>
<tr>
<td>H—I</td>
<td>295</td>
<td>Strong</td>
</tr>
</tbody>
</table>
The more oxygen present in the polyatomic ion of an oxyacid, the **stronger** its acid **WITHIN** that group. That’s a trend, but not an explanation. So, why? First, notice that the H of the acid is bound to an oxygen and NOT any other nonmetal present. Oxygen is very electronegative and attracts the electrons of the O–H bonds toward itself. If you add more oxygens, then this effect is magnified and there is increasing electron density in the region of the molecule that is opposite the H. The added electron density weakens the bond, thus less energy is required to break the bond and the acid dissociates more readily which we describe as “strong”.

![Image of electron density](image.png)

**STRONG BASES**

- Hydroxides OR oxides of IA and IIA metals (except Mg and Be)
  - 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>Table 14.8 Several Series of Oxyacids and Their $K_a$ Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxacid</strong></td>
</tr>
<tr>
<td>ClO$_4^-$</td>
</tr>
<tr>
<td>ClO$_3^-$</td>
</tr>
<tr>
<td>ClO$_2^-$</td>
</tr>
<tr>
<td>ClO$_2^-$</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>H$_2$SO$_3$</td>
</tr>
<tr>
<td>HNO$_3$</td>
</tr>
<tr>
<td>HNO$_2$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 14.1 Various Ways to Describe Acid Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Property</strong></td>
</tr>
<tr>
<td>$K_a$ value</td>
</tr>
<tr>
<td>Position of the dissociation</td>
</tr>
<tr>
<td>(ionization) equilibrium</td>
</tr>
<tr>
<td>Equilibrium concentration of</td>
</tr>
<tr>
<td>$H^+$ compared with original</td>
</tr>
<tr>
<td>concentration of HA</td>
</tr>
<tr>
<td>Strength of conjugate base</td>
</tr>
</tbody>
</table>
WEAK ACIDS AND BASES:

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

That means a equilibrium is established and it lies far to the left (reactant favored). The equilibrium expression for acids is known as the $K_a$ (the acid dissociation constant). It is set up the same way as any other equilibrium expression. 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, the COOH group, like acetic acid and benzoic acid.

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

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} << 1$$

Write the $K_a$ expression for acetic acid. (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 $\text{N}$ forms a bond with a $\text{H}^+$. Most weak bases involve $\text{N}$. 

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

$$K_b = \frac{[HB^+][OH^-]}{[B]} \ll 1$$

for weak base reactions: $\text{B + H}_2\text{O} \rightleftharpoons \text{HB}^+ + \text{OH}^-$

- Write the $K_b$ expression for ammonia.

- 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: $\text{H}^+$ and $\text{H}_2\text{O}^+$ 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.*)

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Conjugate Acid</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>NH$_4^+$</td>
<td>1.8 x 10$^{-5}$</td>
</tr>
<tr>
<td>Methylamine</td>
<td>CH$_3$NH$_2$</td>
<td>CH$_3$NH$_3^+$</td>
<td>4.38 x 10$^{-4}$</td>
</tr>
<tr>
<td>Ethylamine</td>
<td>C$_2$H$_5$NH$_2$</td>
<td>C$_2$H$_5$NH$_3^+$</td>
<td>5.6 x 10$^{-4}$</td>
</tr>
<tr>
<td>Aniline</td>
<td>C$_6$H$_5$NH$_2$</td>
<td>C$_6$H$_5$NH$_3^+$</td>
<td>3.8 x 10$^{-10}$</td>
</tr>
<tr>
<td>Pyridine</td>
<td>C$_5$H$_4$N</td>
<td>C$_5$H$_5$NH$^+$</td>
<td>1.7 x 10$^{-9}$</td>
</tr>
</tbody>
</table>

**Exercise 3**

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

H$_2$O, F$^-$, Cl$^-$, NO$_2^-$, and CN$^-$.

$\text{Cl}^- < \text{H}_2\text{O} < \text{F}^- < \text{NO}_2^- < \text{CN}^-$
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 in a billion water molecules are ionized at any instant!*

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

- The equilibrium expression used here is referred to as the **autoionization constant for water,** \(K_w\)
- In pure water or dilute aqueous solutions, the concentration of water can be considered to be a constant (55.6 \(M\)), so we include that with the equilibrium constant and write the expression as:

\[
K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.008 \times 10^{-14} \text{ at } 25^\circ\text{C} = K_a \times K_b
\]

- Knowing this value allows us to calculate the \(\text{OH}^-\) and \(\text{H}^+\) concentration for various situations.
- \([\text{OH}^-] = [\text{H}^+]\) solution is neutral (in pure water, each of these is \(1.0 \times 10^{-7}\))
- \([\text{OH}^-] > [\text{H}^+]\) solution is basic
- \([\text{OH}^-] < [\text{H}^+]\) solution is acidic

**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 below is exothermic or endothermic.

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

b. Calculate \([\text{H}^+]\) and \([\text{OH}^-]\) in a neutral solution at 60°C.

A: endothermic

\[B: [\text{H}^+] = [\text{OH}^-] = 3 \times 10^{-7} \text{ M}\]
The pH Scale

- Used to designate the $[H^+]$ in most aqueous solutions where $[H^+]$ is small.
  
  \[
  \text{pH} = -\log [H^+]
  \]
  
  \[
  \text{pOH} = -\log [OH^-]
  \]
  
  \[
  \text{pH} + \text{pOH} = 14
  \]

If pH is between zero and 6.999, the solution is acidic, if pH is 7.000, the solution is neutral and if the pH is above 7.000, the solution is basic.

- Reporting the correct number of sig. figs on a pH is problematic since it is a logarithmic scale. The rule is to report as many decimal places on a pH as there are in the least accurate measurement you are given.

- Example: The problem states a 1.15 $M$ solution blah, blah, blah. That is your cue to report a pH with 3 decimal places. If the problem had stated a 1.2 $M$ solution blah, blah, blah, then you would report your calculated pH to 2 decimal places. How did this ever get started? If you care…read the next bullet…otherwise go directly to Exercise 6!

- In the old days, before calculators (Can you imagine?), students used log tables to work problems involving logarithms. If the logarithm was 7.45, then the “7” was the characteristic and the “.45” part was the mantissa. In fact, it is the mantissa that communicates the accuracy of the measurement. The characteristic is simply a place holder.

<table>
<thead>
<tr>
<th>pH</th>
<th>Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Pure water</td>
</tr>
<tr>
<td>6</td>
<td>Milk</td>
</tr>
<tr>
<td>5</td>
<td>Vinegar</td>
</tr>
<tr>
<td>4</td>
<td>Lemon juice</td>
</tr>
<tr>
<td>3</td>
<td>Stomach acid</td>
</tr>
<tr>
<td>2</td>
<td>1 $M$ HCl</td>
</tr>
<tr>
<td>1</td>
<td>1 $M$ NaOH</td>
</tr>
</tbody>
</table>

Exercise 6: Calculating $[H^+]$ and $[OH^-]$

Calculate either the $[H^+]$ or $[OH^-]$ from the information given for each of the following solutions at 25°C, and state whether the solution is neutral, acidic, or basic.

a. $1.0 \times 10^{-5} \, M \, OH^-$

b. $1.0 \times 10^{-7} \, M \, OH^-

c. $10.0 \, M \, H^+$

A: $[H^+] = 1.0 \times 10^{-9} \, M$, basic
B: $[H^+] = 1.0 \times 10^{-7} \, M$, neutral
C: $[OH^-] = 1.0 \times 10^{-15} \, M$, acidic
Exercise 7  
Calculating pH and pOH

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

a.  \(1.0 \times 10^{-3} \ M \ OH^-\)

b.  \(1.0 \ M \ H^+\)

A:  \(pH = 11.00\)
   \(pOH = 3.00\)
B:  \(pH = 0.00\)
   \(pOH = 14.00\)

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} \ M\]  
\([OH^-] = 2.6 \times 10^{-7} \ M\]

Exercise 9  
\textbf{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:  \(pH = 10.00\)
The Chemistry of Acids & Bases

Exercise 10       The pH of Strong Bases

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

\[
pH = 12.70
\]

Calculating pH of Weak Acid Solutions

Calculating pH of weak acids involves setting up an equilibrium. Always start by writing the balanced 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 TABLE method you learned in general equilibrium!

Example

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

\[
\begin{align*}
\text{Reaction} & \quad \text{HC}_2\text{H}_3\text{O}_2 \quad \rightleftharpoons \quad \text{H}^+ \quad + \quad \text{C}_2\text{H}_3\text{O}_2^- \\
\text{Initial} & \quad 1.00 \times 10^{-4} \quad \quad 0 \quad \quad 0 \\
\text{Change} & \quad -x \quad +x \quad +x \\
\text{Equilibrium} & \quad (1.00 \times 10^{-4}) - x \quad x \quad x
\end{align*}
\]

\[
K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{x^2}{1 \times 10^{-4} - x}
\]

See that \(-x\) term in the denominator? That is your invitation to cross multiply and distribute the \(K_a\) value across the term so that you get \(x^2 = 1.8 \times 10^{-9} - 1.8 \times 10^{-5}x\); collect like terms and use either the solver on your graphing calculator or a quadratic formula solving program you’ve loaded on your calculator (all of this to avoid arithmetic mistakes!) to solve for \(x\). You should determine that \(x = [\text{H}^+] = 3.44 \times 10^{-4}\) and that the pH = \(- \log (3.44 \times 10^{-4}) = 3.46\) (2 SF).

Often, the \(-x\) term in a \(K_a\) expression can be neglected. That simplifies the math tremendously since you are now spared the tedium of having to use the quadratic formula.

How do you know when to neglect \(x\)? Easy. Look at the original concentration and compare it to 100 \(K_a\) (or 100 \(K_b\)). If the initial concentration is large by comparison, you can neglect subtracting the \(x\) term. We could not neglect \(x\) in the example we just worked since 100 \(K_a\) for acetic acid would equal 1.8 × 10^{-3} or 0.0018 which is too close to our initial acid concentration of 0.0001.
Need proof?

Suppose our initial concentration had been 0.10 \( M \) for the acetic acid in the example problem we just worked. For acetic acid, \( 100K_a = 1.8 \times 10^{-3} \) or 0.0018. That’s essentially subtracting zero from 0.10 \( M \). Aside from that if you did subtract it, you’d still follow the “least decimal place” subtraction sig. fig. rule and report 0.10 \( M \) as your answer to the subtraction.

OK, I’ll humor you and apply the quadratic formula to the example we just worked changing the initial concentration to 0.10 \( M \). First I’ll do the quadratic formula and then I’ll work it by “neglecting \( x \”).

**Example**

*Calculate the pH of a 10.10 \( M \) solution of acetic acid. The \( K_a \) of acetic acid is \( 1.8 \times 10^{-5} \).*

<table>
<thead>
<tr>
<th>Reaction</th>
<th>( \text{HC}_2\text{H}_3\text{O}_2 )</th>
<th>( \rightleftharpoons )</th>
<th>( \text{H}^+ )</th>
<th>+</th>
<th>( \text{C}_2\text{H}_3\text{O}_2^- )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td>0</td>
<td>0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td>(-x)</td>
<td>(+x)</td>
<td>(+x)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.10 (-x)</td>
<td>(x)</td>
<td>(x)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x} \]

By cross multiplying and NOT neglecting \( x \), you get \( x^2 = 1.8 \times 10^{-6} - 1.8 \times 10^{-5}x \); collect like terms and use either the solver on your graphing calculator or a quadratic formula solving program you’ve loaded on your calculator (all of this to avoid arithmetic mistakes!) to solve for \( x \). You should determine that \( x = [\text{H}^+] = 0.0013327 \) (way too many sig. figs, I know!)

and that the pH = \( -\log (0.0013327) = 2.88 \) (2 SF)

Had we “neglected \( x \)” , the math simplifies to

\[ K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5} = \frac{x^2}{0.10 - x} \]

\( x^2 = 1.8 \times 10^{-6} \)

So, take the square root of each side to get

\[ \sqrt{x^2} = \sqrt{1.8 \times 10^{-6}} \]

\[ x = 0.001341 = [\text{H}^+] \]

pH = \( -\log (0.001341) = 2.87 \) (2 SF) which is mighty, mighty close, so it is a really good approximation.

So, what’s the good news? The AP exam does not have equilibrium problems that require the quadratic formula. Feel better? No promises about your homework, though! 😊
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) 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.

\[
pH = 4.23
\]
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.

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$_2$ ($K_a = 4.0 \times 10^{-4}$). Also calculate the concentration of cyanide ion (CN$^-$) in this solution at equilibrium.

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

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.

a. 1.00 $M$ HC$_2$H$_3$O$_2$

b. 0.100 $M$ HC$_2$H$_3$O$_2$

A: = 0.42 %

B: = 1.3 %
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!

Exercise 15  The pH of Weak Bases I

Calculate the pH for a 15.0 $M$ solution of 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 ($K_b = 4.38 \times 10^{-4}$).

\[ pH = 12.32 \]

**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.

    \[
    \begin{align*}
    \text{H}_3\text{PO}_4(\text{aq}) + \text{H}_2\text{O}(l) &\rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{H}_2\text{PO}_4^-(\text{aq}) & K_{a1} = 7.5 \times 10^{-3} \\
    \text{H}_2\text{PO}_4^-(\text{aq}) + \text{H}_2\text{O}(l) &\rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{HPO}_4^{2-}(\text{aq}) & K_{a2} = 6.2 \times 10^{-8} \\
    \text{HPO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(l) &\rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) & K_{a3} = 4.8 \times 10^{-13}
    \end{align*}
    \]

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

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>$K_{a1}$</th>
<th>$K_{a2}$</th>
<th>$K_{a3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphoric acid</td>
<td>H$_3$PO$_4$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>$6.2 \times 10^{-8}$</td>
<td>$4.8 \times 10^{-13}$</td>
</tr>
<tr>
<td>Arsenic acid</td>
<td>H$_3$AsO$_4$</td>
<td>$5 \times 10^{-3}$</td>
<td>$8 \times 10^{-8}$</td>
<td>$6 \times 10^{-10}$</td>
</tr>
<tr>
<td>Carbonic acid</td>
<td>H$_2$CO$_3$</td>
<td>$4.3 \times 10^{-7}$</td>
<td>$5.6 \times 10^{-13}$</td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H$_2$SO$_4$</td>
<td>Large</td>
<td>$1.2 \times 10^{-2}$</td>
<td></td>
</tr>
<tr>
<td>Sulfurous acid</td>
<td>H$_2$SO$_3$</td>
<td>$1.5 \times 10^{-2}$</td>
<td>$1.0 \times 10^{-7}$</td>
<td>$10^{-19}$</td>
</tr>
<tr>
<td>Hydrogen sulfide</td>
<td>H$_2$S</td>
<td>$1.0 \times 10^{-7}$</td>
<td>$1.0 \times 10^{-5}$</td>
<td>$10^{-19}$</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>H$_2$C$_2$O$_4$</td>
<td>$6.5 \times 10^{-2}$</td>
<td>$6.1 \times 10^{-5}$</td>
<td>$10^{-19}$</td>
</tr>
<tr>
<td>Ascorbic acid</td>
<td>H$_2$C$_6$H$_8$O$_6$</td>
<td>$7.9 \times 10^{-5}$</td>
<td>$1.6 \times 10^{-12}$</td>
<td>$10^{-19}$</td>
</tr>
</tbody>
</table>

*The $K_{a3}$ value for H$_2$S is very uncertain. Because it is so small, the $K_{a3}$ value is very difficult to measure accurately.*
Except for H₂SO₄, 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 H₂SO₄ 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 H₃PO₄ solution and the equilibrium concentrations of the species H₃PO₄, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻.

<table>
<thead>
<tr>
<th>Specie</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃PO₄</td>
<td>4.8 M</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>0.19 M</td>
</tr>
<tr>
<td>HPO₄²⁻</td>
<td>6.2 × 10⁻₈ M</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>1.6 × 10⁻¹₉ M</td>
</tr>
</tbody>
</table>

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

Calculate the pH of a 1.0 M H₂SO₄ solution.

pH = 0.00
Exercise 19  

The pH of a Sulfuric Acid

Calculate the pH of a $1.0 \times 10^{-2} \text{M} \text{H}_2\text{SO}_4$ solution.

\[ \text{pH} = 1.84 \]

ACID-BASE PROPERTIES OF SALTS: HYDROLYSIS (Splitting of water)

Salts are produced when an acid and base react. Salts are **not** always neutral. Some hydrolyze with water to produce aqueous solutions with pHs other than 7.00.

- **Neutral Salts**—Salts that are formed from the cation of a strong base reacting with the anion of a strong acid are neutral. Beware of solubility issues! One salt such is NaNO\textsubscript{3}. Think about which acid reacted with which base to form the salt...if both the acid and base are strong, then the salt is neutral.

- **Basic Salts**—Salts that are formed from the cation of a strong base reacting with the anion of a weak acid are basic. Again, beware of solubility issues! The anion hydrolyzes the water molecule to produce hydroxide ions and thus a basic solution. $\text{K}_2\text{C}_2\text{H}_3\text{O}_2$ should be basic since $\text{C}_2\text{H}_3\text{O}_2^-$ is the CB of the weak acid $\text{HC}_2\text{H}_3\text{O}_2^-$ while $\text{K}^+$ does not hydrolyze appreciably.

\[
\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{HC}_2\text{H}_3\text{O}_2
\]

strong base \hspace{1cm} weak acid

- **Acidic Salts**—Salts that are formed from the cation of a weak base reacting with the anion of a strong acid are acidic. The cation hydrolyzes the water molecule to produce hydronium ions and thus an acidic solution. NH\textsubscript{4}Cl should be weakly acidic, since NH\textsubscript{4}\textsuperscript{+} hydrolyzes to give an acidic solution, while Cl\textsuperscript{-} does not hydrolyze.

\[
\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3
\]

strong acid \hspace{1cm} weak base

- 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.

<table>
<thead>
<tr>
<th>Table 14.5</th>
<th>Qualitative Prediction of pH for Solutions of Salts for Which Both Cation and Anion Have Acidic or Basic Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_a &gt; K_b$</td>
<td>pH &lt; 7 (acidic)</td>
</tr>
<tr>
<td>$K_a &lt; K_b$</td>
<td>pH &gt; 7 (basic)</td>
</tr>
<tr>
<td>$K_a = K_b$</td>
<td>pH = 7 (neutral)</td>
</tr>
</tbody>
</table>
Here’s how to think this through:

1. Look at the salt and ask yourself which acid and which base reacted to form it?

2. Ask yourself “strong or weak?” for each.

3. Embrace the fact that “strong wins” and predict whether the salt is acidic or basic based on that victory.
   a. If you predict basic, write $\rightleftharpoons \text{OH}^-$
   b. If you predict acidic, write $\rightleftharpoons \text{H}^+$

4. Relish in the fact that “strong is a spectator”. Which means the remaining ion of the salt is the reactant along with water.

5. Write water as HOH to make it easier to see how the hydroxide or hydrogen ion was formed.

Example:
Question: What is the qualitative pH of Fe(NO$_3$)$_3$?

1. Which acid reacted? Nitric
2. Strong or weak? Strong
3. Which base reacted? Iron(III) hydroxide
4. Strong or weak? Weak

Strong wins! $\therefore$ acidic so we write:

\[
\text{+ HOH } \rightleftharpoons \text{H}^+ \quad \text{to get started}
\]

Strong is also a spectator so, cross out the spectator and the remaining ion is the other reactant; Fe(NO$_3$)$_3$

Complete hydrolysis reaction: \[\text{Fe}^{3+} + 3 \text{ HOH} \rightleftharpoons 3 \text{ H}^+ + \text{Fe(OH)}_3\]

<table>
<thead>
<tr>
<th>Exercise 20</th>
<th>The Acid-Base Properties of Salts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Predict whether an aqueous solution of each of the following salts will be acidic, basic, or neutral. Prove with appropriate equations.</td>
<td></td>
</tr>
</tbody>
</table>

a. NaC$_2$H$_3$O$_2$

b. NH$_4$NO$_3$

c. Al$_2$(SO$_4$)$_3$
Exercise 21  
**Salts as Weak Bases**

Calculate the pH of a 0.30 M NaF solution. The $K_a$ value for HF is $7.2 \times 10^{-4}$.

$$\text{pH} = 8.31$$

Exercise 22  
**Salts as Weak Acids I**

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

$$\text{pH} = 5.13$$

Exercise 23  
**Salts as Weak Acids II**

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

$$\text{pH} = 3.43$$
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!

BF₃--most famous of all!!

Exercise 24
Tell whether each of the following is a Lewis acid or base: Draw structures as proof.
- a) PH₃
- b) BCl₃
- c) H₂S
- d) SF₄
Exercise 25  Lewis Acids and Basis

For each reaction, identify the Lewis acid and base.

a. \( \text{Ni}^{2+} (\text{aq}) + 6\text{NH}_3(\text{aq}) \rightarrow \text{Ni}((\text{NH}_3)_6)^{2+} (\text{aq}) \)

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