Ch. 16 Acids and Bases
Acid/base character (pH) of a solution has enormous impact
  a. lake biosystem (acid rain)
  b. farming/gardening (soil pH, alkalinity, etc)
  c. rusting/corrosion
  d. biology
    - cells, proteins, blood, enzymes, hormones need very tight pH control
    - Most bio reaction mechanisms involve H⁺ transfer \(\rightarrow [H^+]\) has huge impact on rates

16.1 Bronsted-Lowry Concept of Acids/Bases

<table>
<thead>
<tr>
<th>Acid</th>
<th>Lewis Definition</th>
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<tbody>
<tr>
<td>H⁺ donor</td>
<td>Lone-pair acceptor</td>
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<tr>
<td>H⁺ acceptor</td>
<td>Lone-pair donor</td>
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</tbody>
</table>

Strong Acid and water:

\[
\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- \\
\text{acid (donor)} \quad \text{base (acceptor)} \\
\text{H}^+ \quad \text{H}^+ \\
\text{conjugate} \quad \text{conjugate}
\]

Weak Base and water:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \\
\text{base (donor)} \quad \text{acid (acceptor)} \\
\text{H}^+ \quad \text{H}^+ \\
\text{conjugate} \quad \text{conjugate}
\]

Notes:
1. An **acid loses** an H⁺ and gets more negative
   - A neutral acid becomes an **anion** after loss of H⁺ \(\text{HCl} \rightarrow \text{Cl}^-\)
   - A cationic acid becomes neutral after loss of H⁺ \(\text{H}_3\text{O}^+ \rightarrow \text{H}_2\text{O}\)

2. A **base gains** an H⁺ and gets more positive
   - A neutral base becomes a **cation** after gain of H⁺ \(\text{H}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+\)
   - An anionic base becomes neutral after gain of H⁺ \(\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}\)

**The change in either charge or number of H's can help identify whether a chemical is functioning as an acid or a base.**

3. Every base needs a lone pair which gets used to bond to the new hydrogen
   - The two electrons involved in the new bond to hydrogen always come from an electron pair on the base

4. Water can function as either a base (accepting an H⁺ when an acid is placed in water) or as an acid (donating an H⁺ when a base is placed in water)
5. In every acid-base reaction, you must have both an acid (a chemical functioning as the H⁺ donor) and also a base (a lone-pair donating chemical functioning as the H⁺ acceptor)
   - An acid can’t give unless there is some basic lone-pair to take.....

Terminology: H⁺ = “proton”

Conjugate Acid-Base Pairs
Structures that differ by one H and one charge unit are referred to as conjugate acid-base pairs

<table>
<thead>
<tr>
<th>Conjugate Acid</th>
<th>Conjugate Base</th>
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<tbody>
<tr>
<td>HF</td>
<td>F⁻</td>
<td>H₂O³⁺</td>
<td>HO⁻</td>
</tr>
<tr>
<td>HCl</td>
<td>Cl⁻</td>
<td>H₂O</td>
<td>NH₄⁺</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>HSO₄⁻</td>
<td>NH₄⁺</td>
<td>NH₃</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
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</tr>
</tbody>
</table>

1. Draw the conjugate bases
   a. HCN
   b. HBr
   c. CH₄

2. Draw the conjugate acids
   a. SO₄²⁻
   b. NH₃
   c. Cl⁻
   d. HSO₄⁻ (not H₂SO₄)

Relative Strengths of Acids and Bases

- Stronger acids have weaker conjugate bases and weaker acids have stronger conjugate bases
- Stronger bases have weaker conjugate acids and weaker bases have stronger conjugate acids
Conjugate Pairs in Acid-Base Reactions and Acid-Base Equilibria

1. Note: Some acid-base reactions go entirely to the product side, or stay entirely on left side.
2. But many acid-base reactions involve equilibria, in which a proton is shuffling back and forth from side to side.
3. In the example shown, a proton (H\(^{+}\)) jumps back and forth between F and O.
   a. Going from left to right, F is the giver (HF = acid) and O the acceptor (H\(_2\)O = base)
   b. Returning from right back to left, O is the giver (H\(_3\)O\(^{+}\) = acid) and F the acceptor (F\(^{-}\) = base)

\[
\begin{align*}
\text{HF} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^{+} + \text{F}^{-} \\
\text{a} & \text{b} & \text{a} & \text{b}
\end{align*}
\]

Notes
1. Each side of every acid-base reaction has one thing that functions as an acid and the other as a base. (This is true on the right side as well as on the left side).
2. Every acid-base reaction has 2 conjugate pairs
   a. For the acid on the left, it's conjugate base appears on the right side
   b. For the base on the left, it's conjugate acid appears on the right side.

Problems: For each of the species in the following equilibria, mark whether it functions as an acid or a base?
- For each of the species in the following equilibrium, draw an arrow to it’s conjugate.

\[
\begin{align*}
a. \text{NH}_3 + \text{HClO} & \rightleftharpoons \text{NH}_4^{+} + \text{ClO}^{-} \\
\text{b} & \text{a} & \text{a} & \text{b} \\

b. \text{HCN} + \text{H}_2\text{PO}_3^{-} & \rightleftharpoons \text{H}_3\text{PO}_3 + \text{CN}^{-} \\
\text{a} & \text{b} & \text{a} & \text{b} \\

c. \text{CH}_3\text{NH}_2 + \text{CH}_3\text{OH}_2^{+} & \rightleftharpoons \text{CH}_3\text{NH}_3^{+} + \text{CH}_3\text{OH} \\
\text{b} & \text{a} & \text{a} & \text{b} \\

d. \text{H}_2\text{O} + \text{HSO}_4^{-} & \rightleftharpoons \text{H}_3\text{O}^{+} + \text{SO}_4^{2-} \\
\text{b} & \text{a} & \text{a} & \text{b}
\end{align*}
\]

Notes/Notice:
1. Notice the change in H-count and the change in charge for each of these.
2. The acid on the left always loses a hydrogen and becomes one step unit more negative.
3. The base on the left always gains a hydrogen and becomes more positive.
4. Cations usually function as acids
   - They are positive, and want to get rid of H\(^{+}\) to alleviate positive charge.
5. An anion usually function as a base
   - It usually wants to get more positive, and the negative charge always means it has a lone-pair available.
   - Some exceptions, such as example “d”.
Acid/Base Strength

1. **Strong acids** are better $H^+$ donors than **weaker acids**
   Strong bases are better $H^+$ acceptors than weaker bases

2. Acid/base strength depends on love for $H^+$
   - Consider the conjugate pair of $Z^-$ and $HZ$
     a. High $H^+$ Love: Suppose $Z^-$ really loves $H^+$
        1. Then $Z^-$ is a strong base
           - It aggressively grabs $H^+$ from somebody else
        2. Then $HZ$ is a very weak acid or a total non-acid
           - $Z$ tightly holds onto the $H^+$
           - It doesn’t let anybody else steal $H^+$ unless it’s a base who loves $H^+$ even more
     b. Low $H^+$ Love: Suppose $Z^-$ doesn’t have much love for $H^+$
        1. Then $Z^-$ is a weak base or a totally non-base
           - It’s very weak about grabbing $H^+$ from somebody else
        2. Then $HZ$ is acidic
           - $Z$ is very weak about holding onto the $H^+$
           - Some base who loves $H^+$ more can easily steal the $H^+$ away and leave $Z^-$ behind

3. Love for $H^+$ and the Competition between Competing Bases

   \[ \text{acid} + \text{base} \rightleftharpoons \text{base}^- + \text{acid} \]

   NOTICE: There is one hydrogen, but two things ($Z^-$ and $X^-$) competing for it.
   a. Whichever base loves $H^+$ **more** will be the **stronger base**, and the equilibrium will drive to the opposite direction to the conjugate acid of the strong base
   b. Whichever base loves $H^+$ **less** will lose the competition and remain in its basic form

   1. Strong love for $H^+$ = strong base
   2. Equilibrium goes from strong base to weak base, favors the side where the weaker base lies.
   3. In the same way, the equilibrium always goes from the stronger acid to the weaker acid, and always favors the side with the weaker acid
   4. The weaker acid and weaker base are always on the same side, and the stronger acid and stronger base are always together on the other side
4. Acid-Base Strength and the Direction of Acid-Base Equilibria

*Acid/base reactions always go from stronger acid/base to weaker acid + base

\[
\begin{align*}
\text{HCl} & \quad + \quad \text{NaOH} & \rightarrow & \quad \text{H}_2\text{O} & \quad + & \quad \text{Na}^{+} \text{Cl}^{-} & & \text{K large (K >> 1)} \\
\text{Stronger} & \quad \text{acid} & & & \quad \text{stronger} & \quad \text{base} & & \\
\text{NaOH} & & & & \quad \text{H}_2\text{O} & \quad \text{Na}^{+} & \quad \text{Cl}^{-} & & \\
& & & & & & & & \\
\text{H}_2\text{S} & \quad + \quad \text{F}^{-} & \leftarrow & \quad \text{HF} & \quad + & \quad \text{HS}^{-} & & \text{K small (K < 1)} \\
\text{weaker} & \quad \text{acid} & & & \quad \text{stronger} & \quad \text{base} & & \\
& & & & & & & & \\
\text{HF} & \quad + & \quad \text{Na}^{+} \text{NO}_2^{-} & \rightarrow & \quad \text{Na}^{+} \text{F}^{-} & \quad + & \quad \text{HNO}_2 & & \text{K > 1} \\
\text{HF} & \quad \text{stronger} & & & \quad \text{weaker} & \quad \text{base} & & \\
& & & & & & & & \\
\text{Cl}^{-} & \quad \text{weaker} & & & \quad \text{stronger} & \quad \text{base} & & \\
& & & & & & & & \\
\end{align*}
\]

a. Stronger acid + base always on same side
b. If you know any of relative strengths, can predict sense, K
c. If given K info, can identify weaker/stronger

Problems

1. HF is stronger than HNO\textsubscript{2}. Predict the “direction” of the reaction, and say whether K will be greater or less than 1. (ID each as acid or base)

\[
\begin{align*}
\text{HF} & \quad + \quad \text{Na}^{+} \text{NO}_2^{-} & \quad \rightarrow & \quad \text{Na}^{+} \text{F}^{-} & \quad + & \quad \text{HNO}_2 & & \text{K > 1} \\
\text{HF} & \quad \text{stronger} & & & \quad \text{weaker} & \quad \text{base} & & \\
& & & & & & & & \\
\text{Na}^{+} \text{NO}_2^{-} & & & & \quad \text{Na}^{+} \text{F}^{-} & \quad \text{weaker} & \quad \text{base} & & \\
& & & & & & & & \\
\text{HF} & \quad \text{stronger} & & & \quad \text{weaker} & \quad \text{base} & & \\
& & & & & & & & \\
\text{KNO}_2 & \quad \text{weak} & & & \quad \text{stronger} & \quad \text{base} & & \\
& & & & & & & & \\
\text{HF} & \quad \text{weaker} & & & \quad \text{weak} & \quad \text{acid} & & \\
& & & & & & & & \\
\text{Cl}^{-} & \quad \text{weaker} & & & \quad \text{stronger} & \quad \text{base} & \quad \text{not basic at all} & & \\
& & & & & & & & \\
\end{align*}
\]

2. Predict the “direction” of the reaction, and say whether K will be greater or less than 1.

\[
\begin{align*}
\text{HF} & \quad + \quad \text{Cl}^{-} & \quad \leftarrow & \quad \text{HCl} & \quad + & \quad \text{F}^{-} & & \text{K < 1} \\
\text{HF} & \quad \text{weak} & & & \quad \text{stronger} & \quad \text{base} & & \\
& & & & & & & & \\
\text{Cl}^{-} & \quad \text{weaker} & & & \quad \text{weak} & \quad \text{acid} & & \\
& & & & & & & & \\
\end{align*}
\]

3. Classify each as the weaker or stronger acid or base.

\[
\begin{align*}
\text{HA} & \quad + \quad \text{B}^{-} & \quad \rightarrow & \quad \text{A}^{-} & \quad + & \quad \text{HB} & & \text{K = 10}^3 \\
\text{HA} & \quad \text{stronger} & & & \quad \text{weaker} & \quad \text{base} & & \\
& & & & & & & & \\
\text{B}^{-} & \quad \text{weaker} & & & \quad \text{weaker} & \quad \text{acid} & & \\
& & & & & & & & \\
\text{K} & \quad \text{weaker} & & & \quad \text{weaker} & \quad \text{base} & & \\
& & & & & & & & \\
\end{align*}
\]

4. Classify each as the weaker or stronger acid or base.

\[
\begin{align*}
\text{HCN} & \quad + \quad \text{SO}_4^{2-} & \quad \leftrightarrow & \quad \text{HSO}_4^{-} & \quad + & \quad \text{CN}^{-} & & \text{K = 10}^5 \\
\text{HCN} & \quad \text{weaker} & & & \quad \text{weaker} & \quad \text{base} & & \\
& & & & & & & & \\
\text{SO}_4^{2-} & \quad \text{weaker} & & & \quad \text{weaker} & \quad \text{acid} & & \\
& & & & & & & & \\
\text{K} & \quad \text{stronger} & & & \quad \text{stronger} & \quad \text{base} & & \\
& & & & & & & & \\
\end{align*}
\]

5. **Direct Relationship between strengths of conjugate acid/base**

<table>
<thead>
<tr>
<th>Acid Strength</th>
<th>Strength of Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td>Nonbasic</td>
</tr>
<tr>
<td>Weak</td>
<td>Weak</td>
</tr>
<tr>
<td>Nonacid</td>
<td>Strong base</td>
</tr>
</tbody>
</table>

Note: There is a huge range of strengths within the “weak” category.

<table>
<thead>
<tr>
<th>Strong acids, 100% Ionized in H₂O</th>
<th>Acid</th>
<th>Base</th>
<th>Nonbases</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Cl⁻</td>
<td>HSO₄⁻</td>
<td>H₂O</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
<td>F⁻</td>
</tr>
<tr>
<td>H⁺ (aq) = H₃O⁺</td>
<td>H₂O</td>
<td>CO₃⁻</td>
<td>HCN</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>HCN</td>
<td>OH⁻</td>
<td>H⁺</td>
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<tr>
<td>NH₄⁺</td>
<td>NH₃</td>
<td>H₂O</td>
<td>0⁻</td>
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<tr>
<td>HCO₃⁻</td>
<td>H₂O</td>
<td>OH⁻</td>
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</tbody>
</table>

The weaker the acid, the stronger it's conjugate base
The stronger the acid, the weaker it's conjugate base.

6. **Strong Acids versus Weak Acids versus Nonacids. How do they Differ in Water?**

   a. **Strong acids** ionize completely in water

   \[
   \text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^- 
   \]

   - There is **NO** acid left, no acid where the H and the Cl are bonded.
   - Goes completely to the product side.

   b. **Weak acids** ionize incompletely in water

   - An equilibrium exists
   - Normally only a small amount of product ion is present at equilibrium, and most of the weak acid is in its undissociated form

   \[
   \text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^- \\
   K = 10^{-5}
   \]

   - There is plenty of HF left. But meaningful amounts of \(\text{H}_3\text{O}^+\) and \(\text{F}^-\) ions present.
   - Some “weak” acids are stronger or weaker than others.

   c. **Nonacids:** Don’t ionize at all in water.

   - No equilibrium exists
   - Stays completely on the left side

   \[
   \text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3^- 
   \]
16.1,2 Recognizing Acids

1. **Memorize** Six **strong acids**

\[
\begin{align*}
\text{HCl} & \quad \text{HBr} & \quad \text{HI} & \quad \text{HNO}_3 & \quad \text{H}_2\text{SO}_4 & \quad \text{HClO}_4 \\
\text{Cl}^- & \quad \text{Br}^- & \quad \text{I}^- & \quad \text{NO}_3^- & \quad \text{SO}_4^{2-} & \quad \text{ClO}_4^-
\end{align*}
\]

- Assume all other acids are weak acids
- The conjugate anions of these strong acids are nonbasic

2. Weak acids
   a. Usually formula written with H in front.
      HF\ HCN\ H_2S\ H_2CO_3 \rightarrow \text{acids} \quad \text{H}_2\text{O} \quad \text{weak}
      CH_4\ \text{NH}_3\ \text{SiH}_4 \rightarrow \text{nonacids}

   *Note: NOT ALL H's are acidic!!*

b. Carboxylic acids

\[
\begin{align*}
\text{O} & \quad \text{H} \\
\text{R}\text{C} & \quad \text{O} \\
\text{O} & \quad \text{H}
\end{align*}
\]

- The "R" group can be anything, but is usually hydrocarbon
- The anion is stabilized by resonance
- Carboxylic acids are often written as: CH_3COOH, C_2H_5COOH, etc.

c. Transition-metal Cations: in water they are "hydrated" and function as weak acids
   (Section 16.5, p. 784)
   General: \( M^{+}(\text{H}_2\text{O})_x + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^{+} + M(\text{H}_2\text{O})_{x-1}(\text{OH}) \)
   Ex: \( \text{Fe}^{3+}(\text{H}_2\text{O})_6 + \text{H}_2\text{O} \rightarrow [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^{2+} + \text{H}_3\text{O}^{+} \)
   \( \text{Cu}^{2+}(\text{H}_2\text{O})_4 + \text{H}_2\text{O} \rightarrow [\text{Cu}(\text{H}_2\text{O})_3\text{OH}]^{+} + \text{H}_3\text{O}^{+} \)

d. Ammonium Ions are weak acids (see more under bases, amines)
   - Conjugate acids of neutral amine bases
   - Formal positive charge on nitrogen
   - Unlike most acids, these are cationic species

\text{Ammonium} \quad \text{NH}_4^{+}, \text{CH}_3\text{NH}_3^{+}, (\text{CH}_3)_2\text{NH}_2^{+}, \text{C}_6\text{H}_5\text{NH}_3^{+}, \text{etc.}

\text{Ammonia} \quad \text{NH}_3

\[
\begin{align*}
\text{ammonia} & \quad \text{amines} & \quad \text{ammonium} \\
\text{NH}_3 & \quad \text{H} & \quad \text{NH}_4^{+}
\end{align*}
\]
Recognizing Bases
1. Soluble metal hydroxides ⇒ strong bases
   - All **Group 1 metal hydroxides, many Group 2** ...
   - Group 1 metal hydroxides produce 1 mole of hydroxide per mole of formula
   - Soluble Group 2 metal hydroxides produce 2 moles of hydroxide per formula

<table>
<thead>
<tr>
<th>Group 1</th>
<th>Group 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiOH, NaOH, KOH ...</td>
<td>Ca(OH)₂, Ba(OH)₂ ...</td>
</tr>
</tbody>
</table>

\[
\text{NaOH (aq)} \rightarrow \text{Na}^{+} \text{(aq)} + \text{OH}^{-} \text{(aq)} \text{ (Complete)} \\
1 \text{mole} \quad 1 \text{mole}
\]

\[
\text{Ca(OH)₂ (aq)} \rightarrow \text{Na}^{+} \text{(aq)} + 2 \text{OH}^{-} \text{(aq)} \text{ (Complete)} \\
1 \text{mole} \quad 2 \text{mole}
\]

- most Transition-metal hydroxides have limited solubility and aren’t effectively strong

\[
\text{CuOH(S)} \rightleftharpoons \text{Cu}^{+} \text{(aq)} + \text{OH}^{-} \text{(aq)} \\
1 \text{mole} \quad \text{less than 1 mole} \quad \text{(Incomplete)}
\]

2. Amines: Neutral N Compounds ⇒ weak bases
   Parent: \( \text{H₃N} \cdot + \text{H₂O} \rightleftharpoons \text{OH}^{-} + \text{NH₄}^{+} \)

   - Other amines have N: in common, but replace one or more of the hydrogens with other thing, usually carbon groups

\[\begin{align*}
\text{Amines Bases (examples)} & & \text{Conjugate acids = “Ammonium” Ions} \\
\text{NH₃} & & \text{NH₄}^{+} \\
\text{CH₃NH₂} & & \text{CH₃NH₃}^{+} \\
(CH₃)₂NH & & (CH₃)₂NH₂^{+} \\
\text{C₆H₅NH₂} & & \text{C₆H₅NH₃}^{+}
\end{align*}\]

- N lone pairs accept H⁺
- Amines are the only “neutral bases”. All other bases have anionic charge.
- The conjugate acids are called “ammonium ions” (see earlier)
  - “Amines” = neutral, weakly basic
  - “Ammoniums” = cationic, weakly acidic
- The ammonium ions have formal + charge on N

3. Any conjugate base of a weak acid is weak base

4. Any conjugate base of a non-acid is a strong base
Note: Most Anions are Basic. Whenever you see an anion, consider whether it will be basic!

5. Evaluating the Basicity of Anions
   a. Draw the conjugate acid of the anion
   b. Evaluate the acidity of the conjugate “acid” as strongly acidic, weakly acidic, or nonacidic
   c. Based on the acidity of the acid, decide what the strength of the anion base would be.

<table>
<thead>
<tr>
<th>Conjugate Acid Strength</th>
<th>Strength of Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong acid</td>
<td>Nonbasic</td>
</tr>
<tr>
<td>Weak acid</td>
<td>Weak Base</td>
</tr>
<tr>
<td>Non-acid</td>
<td>Strong base</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Base Strength</th>
<th>Anion</th>
<th>Conjugate Acid</th>
<th>Acid Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak</td>
<td>$\text{F}^-$</td>
<td>$\text{HF}$</td>
<td>$\text{WA}$</td>
</tr>
<tr>
<td>Weak</td>
<td>$\Theta \text{CN}$</td>
<td>$\text{HCN}$</td>
<td>$\text{WA}$</td>
</tr>
<tr>
<td>Weak</td>
<td>$\text{H}_2\text{PO}_4\Theta$</td>
<td>$\text{H}_3\text{PO}_4$</td>
<td>$\text{WA}$</td>
</tr>
<tr>
<td>Non-base</td>
<td>$\text{Cl}^-$</td>
<td>$\text{HCl}$</td>
<td>$\text{SA}$</td>
</tr>
<tr>
<td>Strong base</td>
<td>$\Theta \text{H}$</td>
<td>$\text{H}_2$</td>
<td>non-acid</td>
</tr>
<tr>
<td>Strong base</td>
<td>$\Theta \text{CH}_3$</td>
<td>$\text{CH}_4$</td>
<td>non-acid</td>
</tr>
</tbody>
</table>

Note: Most anions are basic
- Memorize the six anions derived from strong acids that are not basic
- Assume any other anion is basic

Six strong Acids     HCl     HBr     HI     HNO$_3$    H$_2$SO$_4$    HClO$_4$
Six Non-Basic Anions Cl$^-$  Br$^-$  I$^-$  NO$_3^- $  HSO$_4^- $  ClO$_4^-$

Recognizing and Classifying Acid/Base Character of Ionic Formulas
1. Distinguish molecular from ionic formulas
2. For ionics, check each ion separately
   a. Is the cation acidic?
      1. No if it’s a group 1 or group 2 metal cation
      2. Yes if it’s a transition metal cation
      3. Yes if it’s an ammonium cation
   b. Is the anion basic?
      1. No if it’s one of the six non-basic anions derived from strong acids
      2. Yes if it’s any other anion
1. Classify as Strong Acid, Weak Acid, Strong Base, Weak Base, or Non-acid/base
a. HBr       SA
b. HF         WA

c. CH₃CH₂NH₂  WB amine
d. CH₃CH₂COOH  WA carboxylic acid
e. H₂SO₄      SA
f. H₃PO₄      WA
g. HClO       WA
h. ClO⁻       WB HClO is a weak acid
i. Cl⁻        non-base HCl is a strong acid
j. NO₃⁻       non-base HNO₃ is a strong acid
k. O²⁻        strong base HO⁻ is a non acid
l. CH₄        non-acid
m. NaOH       strong base
n. NaF        weak base (F⁻) HF is weak acid
o. KCl        neutral, non-acidic, non-basic
p. NH₄NO₃     WA NH₄⁺
q. FeBr₃       WA Fe³⁺

16.3 Autoionization of water

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

\[
K_w = 1.00 \times 10^{-14} = \left[\text{H}_3\text{O}^{+}\right]\left[\text{OH}^{-}\right]
\]

1. Water is both weakly acidic and basic
2. Amount of ions is teensy but very important
3. \(K_w = 1.00 \times 10^{-14}\) always true
4. If either \([\text{H}_3\text{O}^{+}]\) or \([\text{OH}^{-}]\) known, can calculate other

\[
[\text{H}_3\text{O}^{+}] [\text{OH}^{-}] = 1.00 \times 10^{-14} \quad \text{Memorize!}
\]
16.4 The pH Scale

\[ \text{pH} = -\log[H_3O^+] \quad [H_3O^+] = 10^{-\text{pH}} \]

**Much nicer numbers**

**On calculator:** enter \([H^+]\), hit “log”, and correct the sign from negative to positive

**On calculator:** enter pH, switch the sign from positive to negative, and hit \(10^x\) button (depending on calculator)

1. Higher numberer pH \(\rightarrow\) less \(H^+\), less acidic, more basic
   Lower numbered pH \(\rightarrow\) more \(H^+\), more acidic, more less

   \[
   \begin{array}{ccc}
   \text{pH} & 3.0 & 4.6 & 10.2 \\
   \text{more} & \text{acidic} & \text{less} & \text{acidic}
   \end{array}
   \]

2. pH = 7 neutral
   pH < 7 acidic
   pH > 7 basic

3. pH change of 1 = tenfold change in \([H^+]\)
   Change of 2 = 100-fold change
   pH change of 8 \(\rightarrow\) 4 isn’t double the acid or half the acid, it’s 10 thousand times more!

4. Number of significant figures in \([H^+]\) = number of digits after decimal in pH

   \[
   [H^+] = 3.6 \times 10^{-6} \rightarrow \text{pH} = 5.44
   \]
   2 sig fig \(\rightarrow\) 2 after decimal

5. Small pH changes \(\rightarrow\) death
   - 7.35 < blood < 7.45
   - bio rates are often strongly \(H^+\) catalyzed, with 2\(^{nd}\) or 3\(^{rd}\) order rate dependence on \([H^+]\)

6. \(pOH = -\log[OH^-]\)
   just like pH = -\log \([H^+]\)

   \[
   [OH^-] = 10^{-pOH}
   \]

   just like \([H^+] = 10^{-pH}\)

7. Since \(10^{-14} = [H^+] [OH^-]\) \(\rightarrow\) take negative log of both sides \(\rightarrow\) \(14.00 = \text{pH} + \text{pOH}\)
Skills: interconvert among
$[H^+] \Leftrightarrow [OH^-]$  
$pH \Leftrightarrow pOH$

Problems
1. Find $pH$ for following

a. $[H_3O^+] = 1.0 \times 10^{-4}$  
   $pH = 4.00$

b. $[H^+] = 1.0 \times 10^{-11}$  
   $pH = 11.00$

c. $[H^+] = 3.2 \times 10^{-4}$  
   $pH = 3.49$  
   (notice: lower than 4, not above 4)
   
   a) Use $[H^+] \times [OH^-] = 10^{-14}$  
      or b) $pH + pOH = 14$

   d. $[OH^-] = 1.0 \times 10^{-8}$  
      $pOH = 8.00 \rightarrow pH = 6.00$

   e. $[OH^-] = 5.8 \times 10^{-4}$  
      $pOH = 5.70 \rightarrow pH = 8.30$

   f. $pOH = 8.30$  
      $pH = 5.70$

2. Find $pOH$:

a. $[H^+] = 3.9 \times 10^{-5}$  
   $pH = 4.41$  
   $pOH = 9.59$

b. $[OH^-] = 3.9 \times 10^{-5}$  
   $[OH^-] = 2.56 \times 10^{-10}$

   $pOH = 4.41$

c. $pH = 3.95$  
   $pOH = 10.05$

3. Find both

<table>
<thead>
<tr>
<th>$[H^+]$</th>
<th>$[OH^-]$</th>
<th>$pOH$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.91 \times 10^{-4}$</td>
<td>$5.35 \times 10^{-11}$</td>
<td>10.28</td>
</tr>
<tr>
<td>$1.55 \times 10^{-10}$</td>
<td>$4.46 \times 10^{-5}$</td>
<td>4.19</td>
</tr>
<tr>
<td>$3.5 \times 10^{-8}$</td>
<td>$2.86 \times 10^{-7}$</td>
<td>$pOH = 6.54$</td>
</tr>
<tr>
<td>$4.1 \times 10^{-3}$</td>
<td>$2.44 \times 10^{-12}$</td>
<td>$pOH = 2.39$</td>
</tr>
</tbody>
</table>
16.5 Equilibrium Expressions and Ionization Constants for Acids, Bases.
A. Acids

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

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

Shorthand: HA \rightleftharpoons H^+ + A^- \\

1. Strong acids: ionize completely (\( K_a \) = infinity)
2. Weak acids: \( K_a < 1 \)
3. Larger \( K_a \) \( \Rightarrow \) stronger acid \quad Smaller \( K_a \) \( \Rightarrow \) weaker acid
4. For weak acids, ionizations may be minimal but is still significant
   - for math calculations, the “simplifying assumption” is usually useful
5. Since A\(^-\) and HA are conjugates:
   - larger \( K_a \) \( \Rightarrow \) less basic A\(^-\) (stronger acid \( \rightarrow \) weaker base)
   - smaller \( K_a \) \( \Rightarrow \) more basic A\(^-\) (weaker acid \( \rightarrow \) stronger base)

B. Bases

<table>
<thead>
<tr>
<th>Generic</th>
<th>Base(aq) + H(_2)O(l) \rightleftharpoons OH(^-) (aq) + Base-H(^+) (aq)</th>
<th>Base-H(^+) (aq)</th>
<th>( K_b = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{B}]} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic Base</td>
<td>A(^-) + H(_2)O \rightleftharpoons OH(^-) + HA</td>
<td>Conjugate acid</td>
<td>( K_b = \frac{[\text{OH}^-][\text{HA}]}{[\text{A}^-]} )</td>
</tr>
<tr>
<td>Neutral Amine Base</td>
<td>NH(_3) + H(_2)O \rightleftharpoons OH(^-) + NH(_4)^+</td>
<td>Amine</td>
<td>( K_b = \frac{[\text{OH}^-][\text{NH}_4^+]}{[\text{NH}_3]} )</td>
</tr>
</tbody>
</table>

16.7 Calculations involving \( K_a, K_b, \text{pH}, \text{pOH} \)

A. **Strong Acids**: \([\text{HA}] = [\text{H}^+] \Rightarrow \text{pH} \)
   - Complete ionization \( \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \)
   - To know the concentration of the strong acid is to know the concentration of \( \text{H}^+ \)

B. **Strong Bases**: complete formation of \( \text{OH}^- \)
   - \([\text{NaOH}] = [\text{OH}^-] \Rightarrow \text{pOH}, \text{pH} \)
     - for a group one metal hydroxide (NaOH, etc.), you get exactly as many moles of hydroxide as you put in of NaOH, and \([\text{NaOH}] = [\text{OH}^-] \)
     - \( \text{NaOH} \rightarrow \text{Na}^+ + \text{OH}^- \)
   - For a group two metal hydroxide, you get two moles of hydroxide for every one mole of formula that you put in.
     - \( 1 \text{ Ba(OH)}_2 \rightarrow 1 \text{ Ba}^{2+} + 2 \text{ OH}^- \)
     - \( [\text{OH}^-] = 2 ([\text{Ba(OH)}_2] \)
   - Since \([\text{OH}^-]\) is knowable, you can then plug in, and find pOH, pH, and/or \([\text{H}^+]\)
Some pH Calculations Involving Strong Acids or Bases

1. What is the pH of 1.36×10⁻³ M H₂SO₄?
   \[ [H^+] = 1.36 \times 10^{-3} \]
   Logic: \[\text{pH} = 2.87 \]

2. An HCl solution has pH = 2.16. What is [HCl]?
   Logic: \[\text{pH} \rightarrow [H^+] \rightarrow [HCl] \]
   \[ [H^+] = 0.1 \times 10^{-2} \]
   \[ [HCl] = 6.19 \times 10^{-3} \]

3. What is pH for 0.013 M KOH solution?
   \[ [OH^-] = 0.013 \]
   \[ \rho \text{OH} = 1.89 \]
   Logic: \[\text{pH} = 12.11 \]

4. What is pH for a solution that is 0.013 M in Ca(OH)₂?
   \[ [OH^-] = 0.013 \times 2 = 0.026 \]
   \[ \rho \text{OH} = 1.59 \]
   Logic: \[\text{pH} = 12.41 \]

5. What is the pH if 22 g of Ba(OH)₂ (90 g/mol) is dissolved in 760 mL of water?
   \[ [OH^-] = \frac{22 \text{ g}}{90 \text{ g/mol}} \times \frac{1 \text{ mol}}{2 \text{ mol}} = 0.33 \text{ mol} \]
   \[ [OH^-] = 0.33 \times 2 = 0.66 \text{ mol} \]
   \[ \rho \text{OH} = 0.19 \]
   Logic: \[\text{pH} = 13.81 \]

**C. Weak Acids Calculation: Equilibrium, Kₐ, and pH**  
ICE-able (Section 16.7, p 789-792)

| Two Key Equations | \[ K_a = \frac{[H^+]^2}{[HA]} \] | \[ [H^+] = \sqrt{K_a \cdot [HA]} \] |

1. **Major Application 1:** Given a known \( K_a \), Solve for pH  
When a Known Amount of Weak Acid is Placed in a Known Amount of Water

   **Logic:** Use \( K_a \) \( \rightarrow \) solve for \([H^+]\) \( \rightarrow \) solve for pH

**Steps**
1. Whether it’s given in molarity or not, convert the sample/solvent ratio into Molarity
2. Set up an ICE table
3. Solve for equilibrium \([H^+]\)
   - Use simplifying assumption if \( K_a \) is reasonably small
   - Use another simplifying assumption that the original population of \( H^+ \) is also reasonably small relative to the final, equilibrium amount of \( H^+ \)
4. Use \([H^+]\) to solve for pH

5. Or: If \( K_a \) is small enough so that the simplifying assumption is reasonable, you can directly plug into the equation shown above
Chem 210 Jasperse Ch. 16 Handouts

Initial

\[ [HA]_{\text{init}} \quad 1.0 \times 10^{-7} \quad 0 \]

Change

\[ -x \quad +x \quad +x \]

Equilibrium

\[ [HA]_{\text{init}} \quad \text{small} \]

\[ x + 1.0 \times 10^{-7} \quad \text{small} \]

Equilibrium

After Simplifying

Assumptions

\[ K_a = \frac{[H^+]^2}{[HA]_{\text{init}}} = \frac{x^2}{[HA]_{\text{init}}} \quad \text{or} \quad \frac{[H^+]^2}{[HA]_{\text{init}}} \]

When the simplifying assumptions are used:

\[ K_a = \frac{[H^+]^2}{[HA]_{\text{init}} - [H^+]} \]

When the first simplifying assumption is not used (but the second one is)

\[ [H^+] = \sqrt{K_a \times [HA]_{\text{init}}} \]

Rule of 100:

If \( [HA] < 100 K_a \)

then simplifying assumption is safe.

2. **Major Application 2:** Given a measured pH, solve for \( K_a \) when a known amount of weak acid is placed in a known amount of water.

Logic: Use pH to solve for \( [H^+] \) → solve for \( K_a \)

\[ K_a = \frac{[H^+]^2}{[HA]_{\text{init}}} \]

Learned from pH

\[ \text{Known or knowable} \]

Weak Acid pH/Ka Problems

1. pH → \( K_a \) What is \( K_a \) for an acid if an 0.15 M solution is prepared and found to have pH = 4.86?

Logic:

\[ \begin{align*}
\text{pH} & \rightarrow [H^+] \\
& \rightarrow K_a
\end{align*} \]

Equation(s):

\[ K = \frac{[H^+] [A^-]}{[HA]} = \frac{[H^+]^2}{[HA]} \]

\[ K = (1.38 \times 10^{-5})^2 \]

\[ K = 1.27 \times 10^{-9} \]

\[ HA \rightleftharpoons H^+ + A^- \]

\[ \begin{align*}
0.15 & \quad -x \quad +x \quad +x \\
C & \quad \text{at} \quad 0 \quad \text{M} \\
E & \quad 0.15-x \quad x \quad x
\end{align*} \]
2. $K_a \rightarrow \text{pH}$ What is pH for a 0.15 M solution of an acid with $K_a = 2.2 \times 10^{-6}$?

Logic:

$$K_a \rightarrow [H^+] \rightarrow \text{pH}$$

Equation(s):

$$\begin{align*}
[HA] & \rightleftharpoons H^+ + A^- \\
\text{I} & \quad \text{O} \\
\text{C} & \quad -x \\
\text{E} & \quad x \\
\end{align*}$$

$$\begin{align*}
K_a &= \frac{[H^+][A^-]}{[HA]} \\
&= \frac{1.5 \times 10^{-6}}{0.15} \\
&= 10^{-4} \\
\end{align*}$$

$$\begin{align*}
[H^+]^2 &= 3.3 \times 10^{-7} \\
[H^+] &= 5.74 \times 10^{-4} \\
\text{pH} &= 3.24
\end{align*}$$

3. If an 0.23 M solution of an acid gives pH $= 3.82$, what is $K_a$ for acid?

Logic: $\text{pH} \rightarrow [H^+] \rightarrow K_a$

$$\begin{align*}
\text{pH} &= 3.82, \text{ so } [H^+] = 1.5 \times 10^{-4} \\
K_a &= \frac{(1.5 \times 10^{-4})^2}{0.23} \\
&= 9.8 \times 10^{-8}
\end{align*}$$

4. If a 0.11 M solution has a $K_a = 1.3 \times 10^{-8}$ acid, what is pH?

Logic: $K_a \rightarrow [H^+] \rightarrow \text{pH}$

$$\begin{align*}
[H^+] &= \sqrt{(K_a)[HA]_{init}} = \sqrt{(1.3 \times 10^{-8})(0.11)} = 3.78 \times 10^{-5}
\end{align*}$$

$$\begin{align*}
[H^+] > 100K
\end{align*}$$

**D. Weak Base Calculations involving $K_b$ and pH** (Section 16.7, p 792-793)

$$\begin{align*}
\text{base A} & \underset{\text{H}_2\text{O}}{\rightleftharpoons} \text{conjugate acid HA} + \text{HO}^-
\end{align*}$$

**Initial**

$$\begin{align*}
[A^-]_{init} & \quad 0 \\
\text{Change} & \quad -x \\
\text{Equilibrium} & \quad x \\
\text{Equilibrium} \quad \text{After Simplifying} & \quad x \\
\text{Assumptions} & \quad x
\end{align*}$$

$$\begin{align*}
K_b &= \frac{[HA][OH^-]}{[\text{base}]_{eq}} = \frac{[OH^-]^2}{[\text{base}]_{initial}} \\
& \text{if simplifying assumption good}
\end{align*}$$
When the simplifying assumptions are used:

\[
K_b = \frac{[HO^-]^2}{[A^-]_{init}} \quad [HO^-] = \sqrt{K_b \times [A^-]_{init}}
\]

When the first simplifying assumption is not used but the second one is

\[
K_b = \frac{[HO^-]^2}{[A^-]_{init} - [HO^-]_{base} - x}
\]

\[ [HO^-] \] requires a quadratic solution

### Applications

1. \( pH \rightarrow K_b \)
   - Strategy: \( pH \rightarrow pOH \rightarrow [HO^-] \rightarrow K_b \)
2. \( K_b \rightarrow pH \)
   - Strategy: \( K_b \rightarrow [HO^-] \rightarrow pOH \rightarrow pH \)

### Problems: \( pH \) and \( K_b \)

1. \( pH \rightarrow K_b \) What is \( K_b \) if a 0.123 M solution of a weak base gives \( pH = 10.62 \)?

\[
\begin{align*}
\text{base} & \rightleftharpoons \text{acid} + OH^- \\
\text{I} & .123 0 \sim 0 \\
\text{C} & -x +x +x \\
\text{E} & .123 x x
\end{align*}
\]

Logically: \( pH \rightarrow pOH \rightarrow K_b \)

\[
\begin{align*}
pOH & = 14 - 10.62 = 3.38 \\
\lbrack OH^- \rbrack & = 4.11 \times 10^{-4} = x \\
K_b & = \frac{x^2}{[\text{base}]_{init}} = \frac{(4.11 \times 10^{-4})^2}{0.123} \\
& = 1.41 \times 10^{-6}
\end{align*}
\]

2. \( K_b \rightarrow pH \) If \( K_b \) for a weak base is \( 1.6 \times 10^{-5} \), what is the \( pH \) of a 0.222 M solution of the base?

Logically: \( K_b \rightarrow \lbrack OH^- \rbrack \rightarrow pOH \rightarrow pH \)

\[
\lbrack OH^- \rbrack = \sqrt{(1.6 \times 10^{-5})(0.222)} = 1.88 \times 10^{-3}
\]

\[
pOH = 2.73 \\
pH = 14 - 2.73 = 11.27
\]
E. Relationship Between $K_a$ and $K_b$ for Conjugate acids/bases (Section 16.7, p. 794)

- Review: stronger the acid, weaker the conjugate base (and vice versa)

$K_a \times K_b = 1.0 \times 10^{-14}$  
Review Table 16.2

1. Given one, can solve for other.
2. Tables routinely provide only one; expect you to solve for other
3. Can rank relative strengths of acids (or bases) given info about conjugates

4. Toughest problem: given $K_a$ for conjugate acid, calculate pH for a solution of weak base
   - Logic: $K_a \rightarrow K_b \rightarrow [HO^-] \rightarrow pOH \rightarrow pH$

Derivation of $K_a K_b = 10^{-14}$ (not responsible for derivation, just for interest)

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

So $K_a K_b = \frac{[H_3O^+][A^-][OH^-][HA]}{[HA][A^-]} = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Thus $K_a K_b = K_w = 10^{-14}$

<table>
<thead>
<tr>
<th>Acid Strength</th>
<th>$K_a$</th>
<th>$K_b$</th>
<th>Strength of Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td>$K_a &gt; 1$</td>
<td>$K_b &lt; 1 \times 10^{-14}$</td>
<td>Nonbasic</td>
</tr>
<tr>
<td>Weak</td>
<td>$1 \times 10^{-14} &lt; K_a &lt; 1$</td>
<td>$1 \times 10^{-14} &lt; K_b &lt; 1$</td>
<td>Weak</td>
</tr>
<tr>
<td>Nonacid</td>
<td>$K_a &lt; 1 \times 10^{-14}$</td>
<td>$K_b &gt; 1$</td>
<td>Strong base</td>
</tr>
</tbody>
</table>

Problems Involving Relationship between $K_a$ and $K_b$ for Conjugated Acid/Base

<table>
<thead>
<tr>
<th>Substance</th>
<th>$H_F$</th>
<th>$HN_3$</th>
<th>$HCN$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_a$</td>
<td>$6.8 \times 10^{-4}$</td>
<td>$1.9 \times 10^{-3}$</td>
<td>$4.9 \times 10^{-10}$</td>
</tr>
<tr>
<td>Relative Acidity</td>
<td>2</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Conjugate Base</td>
<td>$F^-$</td>
<td>$N_3^-$</td>
<td>$C_N^-$</td>
</tr>
<tr>
<td>Relative Basicity</td>
<td>2</td>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>$K_b$</td>
<td>$1.4 \times 10^{-11}$</td>
<td>$5.26 \times 10^{-12}$</td>
<td>$2.04 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

1. Rank the acidity for the three weak acids, 1 being strongest. $HN_3 > HF > HCN$

2. Rank the basicity, 1 being the stongest, for:  
   $\text{NaCN}$  $\text{NaF}$  $\text{NaN}_3$
   \[\overset{1}{\text{NaCN}}\]  \[\overset{2}{\text{NaF}}\]  \[\overset{3}{\text{NaN}_3}\]
<table>
<thead>
<tr>
<th>Substance</th>
<th>HF</th>
<th>HN₃</th>
<th>HCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kₐ</td>
<td>6.8 x 10⁻⁴</td>
<td>1.9 x 10⁻³</td>
<td>4.9 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Conjugate Base</td>
<td>Θ⁻</td>
<td>N₃Θ⁻</td>
<td>ΘCN⁻</td>
</tr>
<tr>
<td>Kᵦ</td>
<td>1.47 x 10⁻¹¹</td>
<td>5.26 x 10⁻¹²</td>
<td>2.4 x 10⁻⁵</td>
</tr>
</tbody>
</table>

3. What is Kᵦ for N₃⁻? 

\[ K_a K_b = 1 \times 10^{-14} \]

\[ K_b = \frac{1 \times 10^{-14}}{6.9 \times 10^{-10}} = 1.47 \times 10^{-11} \]

\[ 6.9 > 100 K_b, \text{ so simplify OK} \]

\[ [OH^-] = \sqrt{(1.47 \times 10^{-11})(6.9)} = 1.33 \times 10^{-6} \]

\[ pOH = 5.88 \]

\[ pH = 8.12 \]

4. What is pH for a solution that is 0.12 M in NaF⁻?

Logic: Recognize WBF Situation

\[ K_a \rightarrow K_b \rightarrow [OH^-] \rightarrow pOH \rightarrow pH \]

\[ K_b = \frac{1 \times 10^{-14}}{6.9 \times 10^{-10}} = 1.47 \times 10^{-11} \]

\[ 6.9 > 100 K_b, \text{ so simplify OK} \]

\[ [OH^-] = \sqrt{(1.47 \times 10^{-11})(6.9)} = 1.33 \times 10^{-6} \]

\[ pOH = 5.88 \]

\[ pH = 8.12 \]

5. What is pH for a solution that is 0.20 M in NaCN?

Logic: WBF

\[ K_a \rightarrow K_b \rightarrow [OH^-] \rightarrow pOH \rightarrow pH \]

\[ K_b = \frac{1 \times 10^{-14}}{4.9 \times 10^{-10}} = 2.04 \times 10^{-5} \]

\[ 4.9 > 100 K_b, \text{ so simplify OK} \]

\[ [OH^-] = \sqrt{(2.04 \times 10^{-5})(4.9)} = 2.02 \times 10^{-3} \]

\[ pOH = 2.69 \]

\[ pH = 11.31 \]
C. Polyprotic Acids: More than One H⁺ Available (Section 16.5, p. 783)
H₂SO₄, H₃PO₄, H₂CO₃,...

1. Each H⁺ gets successively less acidic (by > 1000).

<table>
<thead>
<tr>
<th>Relative Acidity</th>
<th>Acid</th>
<th>Kₐ₁</th>
<th>Conjugate Base</th>
<th>Relative Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₃PO₄</td>
<td>10⁻³</td>
<td>H₂PO₄⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂PO₄⁻</td>
<td>10⁻⁸</td>
<td>HPO₄²⁻</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HPO₄²⁻</td>
<td>10⁻¹³</td>
<td>PO₄³⁻</td>
<td></td>
</tr>
</tbody>
</table>

2. As acids in water, only consider the first ionization.
3. When base is added, however, all H⁺'s come off (stoichiometry permitting)
   \[ H₃PO₄ + H₂O \rightarrow H₃O⁺ + H₂PO₄⁻ \]
   But \[ H₃PO₄ + 3 OH⁻ \rightarrow 3 H₂O + PO₄³⁻ \]

4. H₂SO₄: 1st strong, 2nd weak
   
   \[
   \begin{array}{c|c|c|c|c}
   \text{Acid} & \text{Kₐ₁} & \text{Conjugate Base} & \text{Relative Basicity} \\
   \text{H₂SO₄} & 10⁻³ & HSO₄⁻ & \text{Complete} \\
   \text{H₂SO₄} & 10⁻⁶ & SO₄²⁻ & \text{little} \\
   \text{H₂SO₄} & 10⁻⁸ & \text{weak} & \text{little} \\
   \end{array}
   \]

5. Some anions are complex: both acidic and basic!!
   \[
   \begin{array}{c|c|c|c|c}
   \text{Anion} & \text{Kₐ₁} & \text{Conjugate Base} & \text{Relative Basicity} \\
   \text{HCO₃⁻} & 10⁻³ & H⁺ + CO₃²⁻ & \text{strong} \\
   \text{H₂CO₃} & 10⁻⁵ & OH⁻ + H₂CO₃ & \text{weak} \\
   \end{array}
   \]

**Polyprotic Acid/Base Problems**

1. Which is the stronger acid?
   \[
   \begin{array}{c|c|c}
   \text{Acid} & \text{Kₐ₁} & \text{Conjugate Base} \\
   \text{H₃PO₄} & 10⁻³ & H₂PO₄⁻ \\
   \text{H₂SO₄} & 10⁻⁶ & HSO₄⁻ \\
   \end{array}
   \]

2. Which is the stronger base?
   \[
   \begin{array}{c|c|c}
   \text{Anion} & \text{Kₐ₁} & \text{Conjugate Base} \\
   \text{HCO₃⁻} & 10⁻³ & CO₃²⁻ \\
   \text{HSO₄⁻} & 10⁻⁵ & SO₄²⁻ \\
   \end{array}
   \]
16.8 Acid-Base Properties of Salts (Ionic Compounds)

FeCl₂  MgBr₂  NaCN
pH<7  pH=7  pH>7
acidic  neutral  basic

Recall: “salts” formed by acid/base reactions
“salt”=ionic

Example: SA/SB  HCl + NaOH → H₂O + NaCl  neutral
           WA/SB  HF + NaOH → H₂O + NaF  basic
           SA/WB  HCl + NH₃ → NH₄⁺Cl⁻  acidic
           WA/WB  HF + NH₃ → NH₄⁺F⁻  can’t tell

Observations:
1. Salts can be acidic, basic, or neutral.
2. Depends on strengths of acids/bases from which they form.
3. The “ions” in the salts are conjugates; may be acidic or basic!!

A. General Logic to Predict: Identify Ions individually
1. Cations: acidic or neutral
   a. Group I or II cations are neutral
      Li⁺, Na⁺, K⁺, Mg²⁺, Ba²⁺, ...
      No impact on pH
   b. Al³⁺, T-metal cations are acidic (see 16.5 pg. )
      water
      \[ \text{Al}^{3+} \rightarrow [\text{Al}(\text{H}_2\text{O})_6]^{3+} \rightarrow \text{H}^+ + [\text{Al}(\text{OH})(\text{H}_2\text{O})_5]^{2+} \]
      Weak acid
   c. Ammoniums are acidic
      \( \text{NH}_4^+ \), \( \text{CH}_3\text{NH}_3^+ \) etc.

2. Anions: basic or neutral
   a. Neutral: conjugates of strong acids
      Cl⁻, Br⁻, I⁻, NO₃⁻, ClO₄⁻
   b. Basic: conjugates of weak acids (or non acids)
      F⁻, ClO⁻, ...

3. “Amphoteric” anions derived from polyprotic acids: can be acidic or basic
   -not test responsible
   \( \text{HCO}_3^- \), \( \text{H}_2\text{PO}_4^- \), \( \text{HSO}_3^- \)

B. Predicting acidic/neutral/basic (qualitatively)

<table>
<thead>
<tr>
<th>Cation</th>
<th>anion</th>
<th>salt solution</th>
<th>example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neutral</td>
<td>neutral</td>
<td>neutral</td>
<td>NaCl, KNO₃</td>
</tr>
<tr>
<td>Acidic</td>
<td>neutral</td>
<td>acidic</td>
<td>NH₄Cl, Fe(NO₃)₃</td>
</tr>
<tr>
<td>Neutral</td>
<td>basic</td>
<td>basic</td>
<td>NaF, K(ClO)</td>
</tr>
<tr>
<td>Acidic</td>
<td>basic</td>
<td>can’t predict</td>
<td>NH₄F, Fe(N₃)₃</td>
</tr>
</tbody>
</table>

(without K’s)
Predicting Acid/Base Character for Ionic Formulas
1. Predict as acidic, basic, neutral, or can’t tell.
   
   a. $\text{Na}_2\text{SO}_3$
   - $\text{Na}^{+}$ neutral
   
   b. $\text{MgCl}_2$
   - $\text{Mg}^{2+}$ neutral
   - $\text{Cl}^{-}$ nonbase
   - HCl strong
   
   c. $\text{NH}_4\text{CN}$
   - $\text{NH}_4$ acidic
   - $\text{CN}$ weak
   - HCN weak
   
   d. $\text{CoCl}_2$
   - $\text{Co}^{2+}$ acidic
   - $\text{Cl}^{-}$ neutral
   
   e. $\text{NaNO}_3$
   - $\text{Na}^{+}$ neutral
   - $\text{NO}_3^{-}$ neutral
   
   f. $\text{KN}_3$
   - $\text{K}^{+}$ neutral
   - $\text{N}_3^{-}$ basic
   
   g. $\text{AlCl}_3$
   - $\text{Al}^{3+}$ acidic
   - $\text{Cl}^{-}$ neutral
   
   h. $\text{CH}_3\text{NH}_3\text{Br}$
   - $\text{CH}_3\text{NH}_3$ acidic
   - $\text{Br}^{-}$ neutral

2. Rank the following in terms of increasing pH, 1 being the lowest. (ID as strong/weak acid, strong/weak base, or neutral first!)

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>CaF$_2$</td>
<td>ZnBr$_2$</td>
<td>HNO$_3$</td>
<td>KOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na$^+$</td>
<td>Ca$^{2+}$</td>
<td>Zn$^{2+}$</td>
<td>strong</td>
<td>strong</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl$^{-}$</td>
<td>F$^{-}$</td>
<td>Br$^{-}$</td>
<td>acid</td>
<td>base</td>
<td></td>
<td></td>
</tr>
<tr>
<td>neutral</td>
<td>basic</td>
<td>weak</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3</td>
<td>C4</td>
<td>C2</td>
<td>1</td>
<td>5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
16.6 Molecular Structure and Acid/Base Strength
- Why is something strong or weak? Acidic or Basic? Can we predict from structure, without K’s?

A. 3 Factors on Acid Strength
1. **H-A bond strength: stronger → less acidic**
   - Why H-F (strong bond) is weak acid, but H-Cl, H-Br, H-I are strong acids
   - Row 2 bonds (H-F, O-H, N-H, C-H) usually stronger than row 3, 4 analogs
2. H-A polarity
   - Reflects electronegativity and polarity in the bond to the acidic hydrogen
     - CH₄ non polar → nonacidic
     - H-Br polar → acidic
3. Stability of conjugate A⁻
   - -electron love again a factor
   - CH₄ → H⁺ + CH₃⁻ Horrible. Carbon not electronegative, can’t handle
   - HF → H⁺ + F⁻ Way stronger. Fluorine electronegative, can handle

B. Practical Pattern
1. Horizontal Periodic Pattern: Acidity increase left → right
   - CH₄, NH₃, H₂O, HF
   - K_a 10⁻⁵⁰, 10⁻³², 10⁻¹⁴, 10⁴

Note: e⁻ love, electronegativity/bond-polarity, anion stability all agree

Rank: Acidity of: SiH₄, SH₂, HCl, PH₃

2. Vertical Periodic Pattern: Acidity Increases Top → Bottom
   - due to decreasing H-A bond strength (even though contrary to e⁻ love)
   - HF < HCl
   - Weak strong
   - \( H₂O < H₂S < H₂Se \)
   - \( K_a = 10^{-14} < 10^{-9} < 10^{-6} \)

Note: Basicity of conjugates linked!!

Horizontal: \( \ominus NH₂ > F⁻ \)
Vertical: \( F⁻ > Cl⁻ \)
C. “Oxoacids” (Nonmetal hydroxides)

*Many structures have OH  

\[ \text{Z(OH)}_x \text{(O)}_y \]

<table>
<thead>
<tr>
<th>Base</th>
<th>H$_2$CO$_3$ = C(OH)$_2$O</th>
<th>H$_2$SO$_4$ = S(OH)$_2$O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH</td>
<td>weak acid</td>
<td>strong acid</td>
</tr>
</tbody>
</table>

1. **Metals** with OH are **basic**  
   NaOH, Mg(OH)$_2$, etc.  
   NaOH $\rightarrow$ Na$^+$ + HO$^-$

2. **Nonmetals** with OH are **acidic**  
   F-O-H  
   F-O-H $\rightarrow$ H$^+$ + FO$^-

3. Oxoacid **acidity** increases as you move left $\rightarrow$ right across a row

   \[ \text{Si(OH)}_4 < \text{P(OH)}_3 < \text{S(OH)}_2 < \text{Cl(OH)} \]

   - Electron love increases polarity of O-H bond

4. “Extra” Oxygen’s increase acidity

   \[ \text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO} \]
   \[ \text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3 \]

   **Strong**  
   H$_2$SO$_4$, HClO$_3$  
   **Weak**  
   H$_2$CO$_3$, H$_3$PO$_4$, H$_2$SO$_3$

5. Any **Neutral** Oxoacid with $\geq$ 2 extra O’s is a **strong Acid**

   Strong: H$_2$SO$_4$, HClO$_3$  
   Weak: H$_2$CO$_3$, H$_3$PO$_4$, H$_2$SO$_3$

D. Carboxylic Acids: Famous class of oxoacids

E. “Hydrides”

1. M-H metal hydride $\rightarrow$ basic

   \[ \text{NaH} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{NaOH} \]

2. Non-metal “hydrides” neutral or acidic

   CH$_4$

   H-Cl

**Polarity Reversal:** Compare Na-H to H-Cl
Predicting Acid/Base Properties and Trends

1. Which are acidic vs. basic vs. neutral in water?

<table>
<thead>
<tr>
<th></th>
<th>HClO₃</th>
<th>CH₃COOH</th>
<th>CH₃NH₂</th>
<th>Ca(OH)₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>A</td>
<td>A</td>
<td>B</td>
<td>B</td>
</tr>
</tbody>
</table>

2. Rank Acidity (1 strongest)

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>H₂O</th>
<th>H₂SO₄</th>
<th>CH₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>3</td>
<td>1</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

(1) Strong, memory: oxoacid with 2 extra oxygens
(2) HF > H₂O > CH₄, horizontal pattern

3. Rank Acidity (1 strongest)

<table>
<thead>
<tr>
<th></th>
<th>HClO₄</th>
<th>HClO₃</th>
<th>H₂SO₄</th>
<th>H₂SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

(1) More oxygens
(2) Horizontal

4. Rank Acidity (1 strongest)

<table>
<thead>
<tr>
<th></th>
<th>H₂O</th>
<th>H₂S</th>
<th>H₂Se</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S  /</td>
<td>Se</td>
<td></td>
</tr>
</tbody>
</table>

(1) Vertical

5. Rank Acidity (1 strongest)

<table>
<thead>
<tr>
<th></th>
<th>HBr</th>
<th>H₂Se</th>
<th>H₃As</th>
<th>H₄Ge</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

6. Which would be stronger?

HBrO₃⁻ vs HBrO

(1) More oxygens

7. Rank Basicity (1 strongest)

<table>
<thead>
<tr>
<th></th>
<th>ΘCH₃</th>
<th>ΘNH₂</th>
<th>ΘOH</th>
<th>F⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

(1) Horizontal

8. Rank Basicity (1 strongest)

<table>
<thead>
<tr>
<th></th>
<th>HPO₄²⁻</th>
<th>H₂PO₄⁻</th>
<th>HSO₄⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

(1) 1 vs 2: Charge anion of polyprotic
(2) HSO₄⁻ is conjugate of strong acid, not basic
16.10 Lewis Acids and Bases: focus on electron pairs, not \( H^+ \) movement

<table>
<thead>
<tr>
<th>Lewis acid: e- pair acceptor</th>
<th>Lewis base: e- pair donor</th>
<th>Covers “acid-base” chemistry that doesn’t involve ( H^+ )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water as Lewis Base: Uses an Oxygen Lone Pair</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image1" alt="Lewis Base Diagram" /></td>
<td><img src="image2" alt="Lewis Acid Diagram" /></td>
<td></td>
</tr>
<tr>
<td>Water as Lewis Acid: Accepts Lone Pair</td>
<td></td>
<td></td>
</tr>
<tr>
<td><img src="image3" alt="Lewis Acid Diagram" /></td>
<td><img src="image4" alt="Lewis Base Diagram" /></td>
<td></td>
</tr>
</tbody>
</table>

Other Examples

<table>
<thead>
<tr>
<th>a.</th>
<th>b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}^+ )</td>
<td>( \text{H}^- )</td>
</tr>
<tr>
<td><img src="image5" alt="Example a Diagram" /></td>
<td><img src="image6" alt="Example b Diagram" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>c.</th>
<th>d.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{F}_3\text{B}^- )</td>
<td>( \text{Al}^{3+} )</td>
</tr>
<tr>
<td><img src="image7" alt="Example c Diagram" /></td>
<td><img src="image8" alt="Example d Diagram" /></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>e.</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Zn}^{2+} )</td>
</tr>
<tr>
<td><img src="image9" alt="Example e Diagram" /></td>
</tr>
</tbody>
</table>

**Notes:**
1. A “base” must have a lone pair
   (\( \text{F}^-, \text{OH}_2, \text{NH}_3, \ldots \))
2. All anions have lone pairs \( \rightarrow \) Lewis Base potential
3. An “acid” must be able to accept a lone pair
   - all cations can!!
   - some neutrals: \( \text{BF}_3, \text{SO}_2, \ldots \)

**Lewis Acid/Base Problems**
1. Which would not be a Lewis acid?
   \( \text{AlCl}_3, \text{Ti}^{4+}, \text{NO}_3^- \) \( \text{ZnSO}_4 \)

2. Identify the Lewis acid and Lewis Base
   a. \( \text{Fe}^{3+} + 6 \text{H}_2\text{O} \rightarrow [\text{Fe(H}_2\text{O)}_6]^{3+} \)
   b. \( \text{H}^+ + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{NH}_3 \)
   c. \( \text{Br-CH}_3 + \text{I}^- \rightarrow \text{Br}^- + \text{I-CH}_3 \)
   d. \( \text{Ni}^{2+} + 4 \text{N}_3^- \rightarrow [\text{Ni(N}_3)_4]^{2-} \)
CH. 16 Acid-Base Chemistry Math

Key Equations, Numerical Relationships

1. \([H^+][OH^-] = 1.00 \times 10^{-14}\)

2. \(\text{pH} = -\log[H^+]\)

\(\text{pOH} = -\log[OH^-]\)

\([H^+] = 10^{-\text{pH}}\) (on calculator, enter \(-\text{pH}\), then punch the \(10^x\) button)

\([OH^-] = 10^{-\text{pOH}}\) (on calculator, enter \(-\text{pOH}\), then punch the \(10x\) button)

3. \(\text{pH} + \text{pOH} = 14\)

\(\text{pH} = 14 - \text{pOH}\)

**Weak acid problems**

\(K_a = [H^+][A^-]/[HA]\)

When the simplifying assumptions are used:

4. \(K_a = \frac{[H^+]^2}{[HA]_{\text{init}}}\)

5. \([H^+] = \sqrt{K_a \times [HA]_{\text{init}}}\)

When the first simplifying assumption is not used (but the second one is)

6. \(K_a = \frac{[H^+]^2}{[HA]_{\text{init}} - [H^+]}\)

\([H^+]\) requires a quadratic solution

7. Quadratic Equation: for \(ax^2 + bx = c = 0\)

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

**Weak base problems**

\(K_b = [\text{Base-}H^+][OH^-]/[\text{Base}]\)

but when Base is placed in water, \([\text{Base-}H^+] = [A^-]\) so:

8. \(K_b = \frac{[\text{HO}^-]^2}{[\text{Base}]_{\text{init}}}\)

9. \([\text{HO}^-] = \frac{\sqrt{K_b \times [\text{Base}]_{\text{init}}}}{[\text{HO}^-]}\)

When the first simplifying assumption is not used but the second one is

10. \(K_aK_b = 10^{-14}\) for a conjugate acid/base pair.

   Note: This relationship is routinely used when a K value for your acid or base is not provided, but the K value for it’s conjugate is. So get it indirectly.

Some Calculation Logic Scenarios

1. Strong acid \(\rightarrow\) pH  \(\rightarrow\) \([\text{Strong acid}] \rightarrow [H^+] \rightarrow \text{pH}\)

2. Strong base \(\rightarrow\) pH  \(\rightarrow\) \([\text{Strong base}] \rightarrow [\text{HO}^-] \rightarrow \text{pOH} \rightarrow \text{pH}\)

3. Weak acid + \(K_a\) \(\rightarrow\) pH  \(\rightarrow\) \([\text{Weak acid}] + K_a \rightarrow [H^+] \rightarrow \text{pH}\)

4. pH of weak acid \(\rightarrow K_a\)  \(\rightarrow\) pH \(\rightarrow\) solve for \([H^+] \rightarrow K_a\)

5. Weak base + \(K_b\) \(\rightarrow\) pH  \(\rightarrow\) \([\text{Weak base}] + K_b \rightarrow [\text{HO}^-] \rightarrow \text{pOH} \rightarrow \text{pH}\)

6. pH of weak base \(\rightarrow K_b\)  \(\rightarrow\) pH \(\rightarrow\) solve for \([\text{HO}^-] \rightarrow \text{pOH} \rightarrow \text{pH}\)

7. Weak base + \(K_a\) of conjugate acid \(\rightarrow\) pH  \(\rightarrow\) \(K_a \rightarrow K_b \rightarrow [\text{HO}^-] \rightarrow \text{pOH} \rightarrow \text{pH}\)