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 → [H⁺] has huge impact on rates

16.1 Bronsted-Lowry Concept of Acids/Bases

### Bronsted-Lowry Definition

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

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

Base and water: \[ \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + \text{NH}_4^+ \]

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>
<th>Conjugate Acid</th>
<th>Conjugate Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>F⁻</td>
<td>H₃O⁺</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>
<td>H₂O</td>
<td>Cl⁻</td>
</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⁻

Relative Strengths of Acids and Bases

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>Nonbases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong acids, 100%</td>
<td>HCl</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>Ionized in H₂O</td>
<td>H₂SO₄</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>H⁺ (aq) = H₂O⁺</td>
<td>H₂SO₄⁻</td>
<td>H₂O</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>H₂O</td>
<td>H₂SO₄⁻</td>
</tr>
<tr>
<td>H⁺</td>
<td>H₂CO₃⁻</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>H⁺</td>
<td>F⁻</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>C₂⁺</td>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>OH⁻</td>
<td>NH₃</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>OH⁻</td>
<td>CO₃²⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>OH⁻</td>
<td>O²⁻</td>
</tr>
</tbody>
</table>

• 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\(\oplus\)) jumps back and forth between F and O.
   a. Going from left to right, F is the giver (HF = acid) and O the acceptor (\(H_2O\) = base)
   b. Returning from right back to left, O is the giver (\(H_3O\oplus\) = acid) and F the acceptor
      (F\(\ominus\) = base)

\[
\text{HF} + H_2O \rightleftharpoons H_3O\oplus + F\ominus
\]

**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.

  a. \(\text{NH}_3 + \text{HClO} \rightleftharpoons \text{NH}_4\oplus + \text{ClO}\ominus\)

  b. \(\text{HCN} + \text{H}_2\text{PO}_3\ominus \rightleftharpoons \text{H}_3\text{PO}_3 + \text{CN}\ominus\)

  c. \(\text{CH}_3\text{NH}_2 + \text{CH}_3\text{OH}_2\oplus \rightleftharpoons \text{CH}_3\text{NH}_3\oplus + \text{CH}_3\text{OH}\)

  d. \(\text{H}_2\text{O} + \text{HSO}_4\ominus \rightleftharpoons \text{H}_3\text{O}\oplus + \text{SO}_4^{2-}\)

**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\(\oplus\) 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 $\text{H}^+$ donors than **weaker acids**
   
   Strong bases are better $\text{H}^+$ acceptors than weaker bases

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

3. **Love for $\text{H}^+$** and the Competition between Competing Bases

   $\text{HX} \text{ acid} + \text{Z}^- \text{ base} \rightleftharpoons \text{X}^- \text{ base} + \text{HZ} \text{ acid}$

   **NOTICE:** There is one hydrogen, but two things ($\text{Z}^-$ and $\text{X}^-$) competing for it.

   a. Whichever base loves $\text{H}^+$ **more** will be the **stronger base**, and the equilibrium will drive to the opposite direction $\rightarrow$ to the conjugate acid of the strong base
   
   b. Whichever base loves $\text{H}^+$ **less** will lose the competition and remain in its basic form

   

   

   1. Strong love for $\text{H}^+ = \text{strong base}$
   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

**K favors weaker**

\[
\begin{array}{cccc}
\text{HCl} & + & \text{NaOH} & \rightarrow \\
\text{Stronger} & \rightarrow & \text{weaker}
\end{array}
\]

\[
\begin{array}{cccc}
\text{H}_2\text{O} & + & \text{Na} & \text{Cl}^-
\end{array}
\]

K large (K >>1)

\[
\begin{array}{cccc}
\text{H}_2\text{S} & + & \text{F}^- & \leftarrow \\
\text{weaker} & \leftarrow & \text{stronger}
\end{array}
\]

\[
\begin{array}{cccc}
\text{HF} & + & \text{HS}^-
\end{array}
\]

K small (K <1)

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\(_2\). Predict the “direction” of the reaction, and say whether K will be greater or less than 1. (ID each as acid or base)

\[
\text{HF} + \text{Na} \overset{+}{\text{NO}}_2^- \rightarrow \text{Na} \overset{+}{\text{F}}^- + \text{HNO}_2
\]

K 1

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

\[
\text{HF} + \text{Cl}^- \rightarrow \text{HCl} + \text{F}^-
\]

K 1

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

\[
\text{HA} + \text{B}^- \rightarrow \text{A}^- + \text{HB}
\]

K = 10^3

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

\[
\text{HCN} + \text{SO}_4^{2-} \rightarrow \text{HSO}_4^- + \text{CN}^-
\]

K = 10^{-5}
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>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>H₂O</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>F⁻</td>
<td>F⁻</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>NH₃⁻</td>
<td>NH₃⁻</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>CO₃²⁻</td>
</tr>
<tr>
<td>OH⁻</td>
<td>OH⁻</td>
</tr>
<tr>
<td>O²⁻</td>
<td>O²⁻</td>
</tr>
<tr>
<td>H⁻</td>
<td>H⁻</td>
</tr>
<tr>
<td>Nonbases</td>
<td>Nonbases</td>
</tr>
</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 it’s 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 \(\text{H}_3\text{O}^+ + \text{F}^-\) 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**

   - HCl
   - HBr
   - HI
   - HNO₃
   - H₂SO₄
   - HClO₄

   - **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
      - H₂S
      - H₂CO₃ → acids
      - CH₄
      - NH₃
      - SiH₄ → nonacids

   * Note: NOT ALL H’s are acidic!!

   b. Carboxylic acids

   ![Carboxylic acid structure](image)

   - The “R” group can be anything, but is usually hydrocarbon
   - The anion is stabilized by resonance
   - Carboxylic acids are often written as: CH₃COOH, C₂H₅COOH, etc.

c. Transition-metal Cations: in water they are “hydrated” and function as **weak acids** (Section 16.5, p. 784)

   General: \[ M^{\oplus} (H₂O)_x + H₂O \rightleftharpoons H₃O^{\oplus} + M(H₂O)_{x-1}(OH) \]

   Ex: \[ Fe^{3+}(H₂O)_6 + H₂O \rightleftharpoons [Fe(H₂O)₅OH]^{2+} + H₃O^{\oplus} \]

   \[ Cu^{2+}(H₂O)_₄ + H₂O \rightleftharpoons [Cu(H₂O)₃OH]^{\oplus} + H₃O^{\oplus} \]

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

   \[ NH₄^{\oplus}, CH₃NH₃^{\oplus}, (CH₃)₂NH₂^{\oplus}, C₆H₅NH₃^{\oplus}, \text{etc.} \]
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>

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

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

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

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

2. Amines: Neutral N Compounds ⇒ weak bases
   - Parent: \( \text{H}_3\text{N}: + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{NH}_4^+ \)
     - weak base
     - weak acid

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

<table>
<thead>
<tr>
<th>Amines Bases (examples)</th>
<th>Conjugate acids = “Ammonium” Ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{NH}_3 )</td>
<td>( \text{NH}_3^+ )</td>
</tr>
<tr>
<td>( \text{CH}_3\text{NH}_2 )</td>
<td>( \text{CH}_3\text{NH}_2^+ )</td>
</tr>
<tr>
<td>( \text{(CH}_3)_2\text{NH} )</td>
<td>( \text{(CH}_3)_2\text{NH}^+ )</td>
</tr>
<tr>
<td>( \text{C}_6\text{H}_5\text{NH}_2 )</td>
<td>( \text{C}_6\text{H}_5\text{NH}_2^+ )</td>
</tr>
</tbody>
</table>

   - 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 \( \oplus \) charge on N

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

4. **Any conjugate base of a non-acid is a strong base**
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>F⁻</td>
<td>HF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CN⁻</td>
<td>HCN</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>H₃PO₄</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>HCl</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H⁻</td>
<td>H₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃⁻</td>
<td>CH₄</td>
<td></td>
<td></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
- HNO₃
- H₂SO₄
- HClO₄

**Six Non-Basic Anions**
- Cl⁻
- Br⁻
- I⁻
- NO₃⁻
- HSO₄⁻
- ClO₄⁻

**Recognizing and Classifying Acid/Base Character of Ionic Formulas**

1. Distinguish molecular from ionic formulas
2. **For ions, 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
b. HF
c. CH₃CH₂NH₂
d. CH₃CH₂COOH
e. H₂SO₄
f. H₃PO₄
g. HClO
h. ClO⁻
i. Cl⁻
j. NO₃⁻
k. O²⁻
l. CH₄
m. NaOH
n. NaF
o. KCl
p. NH₄NO₃
q. FeBr₃

16.3 Autoionization of water

\[
\text{H}_2\text{O(l)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{OH}^- (\text{aq}) \quad \text{K}_w = 1.00 \times 10^{-14} =
\]

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

\[ [\text{H}_3\text{O}^+] [\text{OH}^-] = 1.00 \times 10^{-14} \quad \text{Memorize!} \]
Neutral: \([\text{H}_3\text{O}^+] = 1 \times 10^{-7} = [\text{OH}^-]\) \(\text{pH} = 7\)

Acidic: \([\text{H}_3\text{O}^+] > 1 \times 10^{-7} > [\text{OH}^-]\) \(\text{pH} < 7\)

Basic: \([\text{H}_3\text{O}^+] < 1 \times 10^{-7} < [\text{OH}^-]\) \(\text{pH} > 7\)

Note: \(\text{H}^+\) vs. \(\text{H}_3\text{O}^+\)

- \(\text{H}^+\) (proton) in water exists as \(\text{H}_3\text{O}^+\) (hydronium).
- But \(\text{H}^+\) is easier to write!
- They are really the same thing.

16.4 The pH Scale

\[
\text{pH} = -\log[\text{H}_3\text{O}^+]
\]

\[
[\text{H}_3\text{O}^+] = 10^{-\text{pH}}
\]

**Much nicer numbers**

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

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

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

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

2. \(\text{pH} = 7\) neutral \hspace{1cm} \(\text{pH} < 7\) acidic \hspace{1cm} \(\text{pH} > 7\) basic

3. \(\text{pH} \) change of \(1\) = tenfold change in \([\text{H}^+]\)
   Change of \(2\) = 100-fold change
   \(\text{pH} \) 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 \([\text{H}^+]\) = number of digits after decimal in \(\text{pH}\)

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

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

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

   \[
   [\text{OH}^-] = 10^{-\text{pOH}} \quad \text{just like} \quad [\text{H}^+] = 10^{-\text{pH}}
   \]

7. Since \(10^{-14} = [\text{H}^+] [\text{OH}^-]\) \(\rightarrow\) take negative log of both sides \(\rightarrow\)

\[
\boxed{14.00 = \text{pH} + \text{pOH}}
\]
Skills: interconvert among $\text{[H}^+\text{]} \leftrightarrow \text{[OH}^-\text{]}$
\[ \text{pH} \leftrightarrow \text{pOH} \]

Problems
1. Find pH for following
   a. $\text{[H}_3\text{O}^+\text{]} = 1.0 \times 10^{-4}$
   b. $\text{[H}^+\text{]} = 1.0 \times 10^{-11}$
   c. $\text{[H}^+\text{]} = 3.2 \times 10^{-4}$
   d. $\text{[OH}^-\text{]} = 1.0 \times 10^{-8}$
   e. $\text{[OH}^-\text{]} = 5.8 \times 10^{-4}$
   f. pOH = 8.30

2. Find pOH:
   a. $\text{[H}^+\text{]} = 3.9 \times 10^{-5}$
   b. $\text{[OH}^-\text{]} = 3.9 \times 10^{-5}$
   c. pH = 3.95

3. Find both $\text{[H}^+\text{]} \quad \text{[OH}^-\text{]}$
   a. pH = 3.72
   b. pH = 9.81
   c. $\text{[H}^+\text{]} = 3.5 \times 10^{-8}$
   d. $\text{[OH}^-\text{]} = 4.1 \times 10^{-3}$

To know any one allows you to find any of the others!
16.5 Equilibrium Expressions and Ionization Constants for Acids, Bases.

A. Acids

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

Shorthand: \( \text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \) \( K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} \)

1. Strong acids: ionize completely \( K_a = \infty \)
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 \( \text{A}^- \) and \( \text{HA} \) are conjugates:
   • larger \( K_a \) \( \Rightarrow \) less basic \( \text{A}^- \) \( \quad \) (stronger acid \( \Rightarrow \) weaker base)
   • smaller \( K_a \) \( \Rightarrow \) more basic \( \text{A}^- \) \( \quad \) (weaker acid \( \Rightarrow \) stronger base)

B. Bases

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

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

A. **Strong Acids:** \( [\text{HA}] = [\text{H}^+] \) \( \Rightarrow \) 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 \( \text{OH}^- \)
   • \( [\text{NaOH}] = [\text{OH}^-] \) \( \Rightarrow \) pOH, pH
     - for a group one metal hydroxide (\( \text{NaOH} \), etc.), you get exactly as many moles of hydroxide as you put in of \( \text{NaOH} \), 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 \times 10^{-3} \text{ M } \text{H}_2\text{SO}_4?

2. An HCl solution has pH = 2.16. what is [HCl]?

3. What is pH for 0.013 M KOH solution?

4. What is pH for a solution that is 0.013 M in Ca(OH)_2?

5. What is the pH if 22 g of Ba(OH)_2 (90 g/mol) is dissolved in 760 mL of water?

C. Weak Acids Calculation: Equilibrium, K_a, and pH  

| Two Key Equations | \( K_a = \frac{[H^+]^2}{[HA]_{init}} \) | \([H^+] = \sqrt{K_a \cdot [HA]}\); |

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
HA $\rightleftharpoons$ H$^+$ + A$^-$

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

Equilibrium

**Equilibrium**
**After Simplifying Assumptions**

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

When the simplifying assumptions are used:

$$K_a = \frac{[H^+]^2}{[HA]_{init}} \quad [H^+] = \sqrt{K_a \times [HA]_{init}}$$

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

$$K_a = \frac{[H^+]^2}{[HA]_{init} - [H^+]} \quad [H^+] \text{ requires a quadratic solution}$$

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 $\rightarrow$ solve for $[H^+]$ $\rightarrow$ solve for $K_a$

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

**Weak Acid pH/$K_a$ Problems**
1. pH $\rightarrow$ $K_a$ What is $K_a$ for an acid if an 0.15 M solution is prepared and found to have pH = 4.86?

Logic:

Equation(s):
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:

Equation(s):

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

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

---

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

\[
\begin{align*}
\text{A}^{-} & \quad + \text{H}_2\text{O} \quad \underset{\text{HA} \quad + \quad \text{HO}^{-}}{\text{equilibrium}} \\
\text{Initial} & \quad \text{[A}^{-}]_{\text{init}} \quad 0 \quad 1.0 \times 10^{-7}
\end{align*}
\]

Change

Equilibrium

**Equilibrium**

After Simplifying

**Assumptions**

\[K_b =\]
When the simplifying assumptions are used:

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

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

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

<table>
<thead>
<tr>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. pH → K_b</td>
</tr>
<tr>
<td>Strategy:</td>
</tr>
<tr>
<td>pH → pOH → [HO⁻] → K_b</td>
</tr>
<tr>
<td>2. K_b → pH</td>
</tr>
<tr>
<td>Strategy:</td>
</tr>
<tr>
<td>K_b → [HO⁻] → pOH → pH</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Problems: pH and K_b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. pH → K_b</td>
</tr>
<tr>
<td>What is K_b if a 0.123 M solution of a weak base gives pH=10.62?</td>
</tr>
<tr>
<td>2. K_b → pH</td>
</tr>
<tr>
<td>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?</td>
</tr>
</tbody>
</table>
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 $K_aK_b=10^{-14}$** (not responsible for derivation, just for interest)

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

So $K_aK_b = \left(\frac{[H_3O^+][A^-]}{[HA]}\right)\left(\frac{[OH^-][HA]}{[A^-]}\right) = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$

Thus $K_aK_b = K_w = 10^{-14}$

**Acid Strength**

<table>
<thead>
<tr>
<th></th>
<th>$K_a$</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td>$K_a &gt; 1$</td>
<td>$K_b &lt; 1 \times 10^{-14}$</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>
</tr>
<tr>
<td>Nonacid</td>
<td>$K_a &lt; 1 \times 10^{-14}$</td>
<td>$K_b &gt; 1$</td>
</tr>
</tbody>
</table>

**Strength of Conjugate Base**

- Nonbasic
- Weak
- Strong base

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

<table>
<thead>
<tr>
<th>Substance</th>
<th>$K_a$</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>$6.8 \times 10^{-4}$</td>
<td>$1.9 \times 10^{-4}$</td>
</tr>
<tr>
<td>HN$_3$</td>
<td>$4.9 \times 10^{-10}$</td>
<td></td>
</tr>
</tbody>
</table>

1. Rank the acidity for the three weak acids, 1 being strongest.

2. Rank the basicity, 1 being the stongest, for: NaN$_3$ NaF NaCN
<table>
<thead>
<tr>
<th>Substance</th>
<th>HF</th>
<th>HN₃</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>Conjugate Base</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$K_b$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

3. What is $K_b$ for $N_3^-$?

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

Logic:

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

Logic:
C. Polyprotic Acids: More than One H⁺ Available (Section 16.5, p. 783)

\[ \text{H}_2\text{SO}_4, \text{H}_3\text{PO}_4, \text{H}_2\text{CO}_3, \ldots \]

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

<table>
<thead>
<tr>
<th>Relative Acidity</th>
<th>Acid</th>
<th>( K_a )</th>
<th>Conjugate Base</th>
<th>Relative Basicity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \text{H}_3\text{PO}_4 )</td>
<td>( 10^{-3} )</td>
<td>( \text{H}_2\text{PO}_4^- )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{H}_2\text{PO}_4^- )</td>
<td>( 10^{-8} )</td>
<td>( \text{HPO}_4^{2-} )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \text{HPO}_4^{2-} )</td>
<td>( 10^{-13} )</td>
<td>( \text{PO}_4^{3-} )</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)
   \[ \text{H}_2\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^- \]
   But \( \text{H}_3\text{PO}_4 + 3 \text{OH}^- \rightarrow 3 \text{H}_2\text{O} + \text{PO}_4^{3-} \)

4. \( \text{H}_2\text{SO}_4 \): 1\textsuperscript{st} strong, 2\textsuperscript{nd} weak

\[ \text{H}_2\text{SO}_4 \rightarrow \text{H}^+ + \text{HSO}_4^- \]
\[ \text{HSO}_4^- \rightarrow 2\text{H}^+ + \text{SO}_4^{2-} \]

<table>
<thead>
<tr>
<th></th>
<th>water</th>
<th>water</th>
<th>Complete</th>
<th>lot</th>
<th>weak</th>
<th>little</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5. Some anions are complex: both acidic and basic!!

\[ \text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \]
\[ \text{H}_2\text{O} \]
\[ \text{OH}^- + \text{H}_2\text{CO}_3 \]

**Polyprotic Acid/Base Problems**

1. Which is the stronger acid?
   \[ \text{H}_3\text{PO}_4 \]
   \[ \text{H}_2\text{PO}_4^- \]
   \[ \text{H}_2\text{SO}_4 \]
   \[ \text{HSO}_4^- \]

2. Which is the stronger base?
   \[ \text{HCO}_3^- \]
   \[ \text{CO}_3^{2-} \]
   \[ \text{HSO}_4^- \]
   \[ \text{SO}_4^{2-} \]
16.8 Acid-Base Properties of Salts (Ionic Compounds)

<table>
<thead>
<tr>
<th></th>
<th>FeCl₂</th>
<th>MgBr₂</th>
<th>NaCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH&lt;7</td>
<td>acidic</td>
<td>neutral</td>
<td>basic</td>
</tr>
<tr>
<td>pH=7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>pH&gt;7</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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
     Al³⁺ → [Al(H₂O)₆]³⁺ ⇌ H⁺ + [Al(OH)(H₂O)₃]²⁺
     Weak acid
   c. Ammoniums are acidic
      NH₄⁺, CH₃NH₃⁺ 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
      HCO₃⁻, H₂PO₄⁻, HSO₃⁻

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>
<tr>
<td></td>
<td></td>
<td>(without K’s)</td>
<td></td>
</tr>
</tbody>
</table>
Predicting Acid/Base Character for Ionic Formulas

1. Predict as acidic, basic, neutral, or can’t tell.

   a. Na$_2$SO$_3$  
   e. NaNO$_3$

   b. MgCl$_2$  
   f. KN$_3$

   c. NH$_4$CN  
   g. AlCl$_3$

   d. CoCl$_2$  
   h. CH$_3$NH$_3$Br

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

   NaCl  CaF$_2$  ZnBr$_2$  HNO$_3$  KOH
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
   
<table>
<thead>
<tr>
<th></th>
<th>CH₄</th>
<th>NH₃</th>
<th>H₂O</th>
<th>HF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kₐ</td>
<td>10⁻⁵₀</td>
<td>10⁻³²</td>
<td>10⁻¹⁴</td>
<td>10⁻⁴</td>
</tr>
</tbody>
</table>

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)

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Strong</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kₐ</td>
<td>10⁻¹⁴</td>
<td>10⁻⁹</td>
</tr>
</tbody>
</table>

Note: Basicity of conjugates linked!!

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

*Many structures have OH \( Z(OH)_x\)

\[
\begin{align*}
\text{KOH} & \quad \text{H}_2\text{CO}_3 = \text{C(OH)}_2\text{O} \quad \text{H}_2\text{SO}_4 = \text{S(OH)}_2\text{O}_2 \\
\text{Base} & \quad \text{weak acid} \quad \text{strong acid}
\end{align*}
\]

1. **Metals** with OH are **basic** (NaOH, Mg(OH)_2, etc.): \( \text{NaOH} \rightarrow \text{Na}^+ + \text{HO}^- \)
2. **Nonmetals** with OH are **acidic** (F-O-H): \( \text{F-O-H} \rightarrow \text{H}^+ + \text{FO}^- \)
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 increases acidity:

\[
\begin{align*}
\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO} \\
\text{Strong} & \quad \text{weak} \\
\text{H}_2\text{SO}_4 > \text{H}_2\text{SO}_3 & \quad \text{strong} \quad \text{weak}
\end{align*}
\]

Why? Extra electron-loving oxygen

1. Stabilizes resulting anion
2. Polarizes O-H
3. Weakens O-H

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

Strong: \( \text{H}_2\text{SO}_4, \text{HClO}_3 \)  
Weak: \( \text{H}_2\text{CO}_3, \text{H}_3\text{PO}_4, \text{H}_2\text{SO}_3 \)

D. Carboxylic Acids: Famous class of oxoacids

E. “Hydrides”

1. M-H metal hydride \( \rightarrow \) basic

\( \text{NaH} + \text{H}_2\text{O} \rightarrow \)

2. Non-metal “hydrides” neutral or acidic

\( \text{CH}_4 \)

\( \text{H-Cl} \)

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

**Why?**

1. Which are acidic vs. basic vs. neutral in water?
   
   HClO₃  CH₃COOH  CH₃NH₂  Ca(OH)₂

2. Rank Acidity (1 strongest)
   
   HF  H₂O  H₂SO₄  CH₄

3. Rank Acidity (1 strongest)
   
   HClO₄  HClO₃  H₂SO₄  H₂SO₃

4. Rank Acidity (1 strongest)
   
   H₂O  H₂S  H₂Se

5. Rank Acidity (1 strongest)
   
   HBr  H₂Se  H₃As  H₄Ge

6. Which would be stronger?
   
   HBrO₃  vs  HBrO

7. Rank Basicity (1 strongest)
   
   CH₃⁻  NH₂⁻  OH⁻  F⁻

8. Rank Basicity (1 strongest)
   
   HPO₄²⁻  H₂PO₄⁻  HSO₄⁻
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>
</tr>
</thead>
<tbody>
<tr>
<td>Covers “acid-base” chemistry that doesn’t involve H(^+)</td>
<td></td>
</tr>
</tbody>
</table>

Water as Lewis Base: Uses an Oxygen Lone Pair

\[
\begin{align*}
\text{Cl-H} & \quad \text{:O-H} & \quad \text{H-O-H} \\
& \quad \text{H} & \\
\end{align*}
\]

Water as Lewis Acid: Accepts Lone Pair

\[
\begin{align*}
\text{HO-H} & \quad \text{:N-H} & \quad \text{H-N-H} \\
& \quad \text{H} & \\
\end{align*}
\]

Other Examples

<table>
<thead>
<tr>
<th>a. (\text{H}^+ \quad \text{:O-H} \quad \text{H-O-H})</th>
<th>b. (\text{H-O:} \quad \text{H_3C-Br} \quad \text{H-O-CH}_3 + \text{Br}^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{F}_3\text{B}) (\text{:F}^\cdot) (\rightarrow) (\text{BF}_4)</td>
<td>(\text{Al}^{3+} \quad \text{:O-H} \quad \left[\text{Al-O-H}\right]^{3+})</td>
</tr>
<tr>
<td>(\text{Zn}^{2+} \quad \text{:N-H} \quad \left[\text{Zn-N-H}\right]^{2+})</td>
<td></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: BF\(_3\), SO\(_2\), …

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. \(\text{Br-CH}_3 + 1^- \rightarrow \text{Br}^- + \text{I-CH}_3\)
   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. \([H^+][HO^-] = 1.00 \times 10^{-14}\)

2. \(pH = -\log[H^+]\)
   \(pOH = -\log[OH^-]\)
   \([H^+] = 10^{pH}\) (on calculator, enter \(-pH\), then punch the 10^x button)
   \([OH^-] = 10^{pOH}\) (on calculator, enter \(-pOH\), then punch the 10^x button)

3. \(pH + pOH = 14\)
   \(pH = 14 - pOH\)

**Weak acid problems**

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

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

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

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

When the simplifying assumptions are used:

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

6. \(K_a = \frac{[H^+]^2}{[HA]_{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**

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

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

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

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

When the simplifying assumptions are used:

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

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

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

11. \(K_aK_b = 10^{-14}\) 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 \(\rightarrow\) Strong acid \(\rightarrow\) [H \(\oplus\)] \(\rightarrow\) pH
2. Strong base \(\rightarrow\) pH \(\rightarrow\) Strong base \(\rightarrow\) [HO \(\ominus\)] \(\rightarrow\) pH \(\rightarrow\) pH
3. Weak acid + \(K_a\) \(\rightarrow\) pH \(\rightarrow\) Weak acid + \(K_a\) \(\rightarrow\) [H \(\oplus\)] \(\rightarrow\) pH
4. pH of weak acid \(\rightarrow\) \(K_a\) \(\rightarrow\) pH \(\rightarrow\) solve for [H \(\oplus\)] \(\rightarrow\) \(K_a\)
5. Weak base + \(K_b\) \(\rightarrow\) pH \(\rightarrow\) Weak base + \(K_b\) \(\rightarrow\) [HO \(\ominus\)] \(\rightarrow\) pH \(\rightarrow\) pH
6. pH of weak base \(\rightarrow\) \(K_b\) \(\rightarrow\) pH \(\rightarrow\) solve for [HO \(\ominus\)] \(\rightarrow\) pH \(\rightarrow\) pH
7. Weak base + \(K_a\) of conjugate acid \(\rightarrow\) pH \(\rightarrow\) Weak base + \(K_a\) of conjugate acid \(\rightarrow\) pH \(\rightarrow\) pH
Simple Acid-Base Concept Map

\[ [H^+] = [HA] \quad \text{strong acid} \]

\[ \text{pH} \quad 14 \quad \text{pOH} \]

\[ [H^+] \quad K_a, \text{[HA] weak acid} \]

\[ [OH^-] \quad K_b, \text{[Base] weak base} \]

\[ \% \text{ ionization} \quad \frac{[H^+]}{HA} \times 100\% \]