Table 16.1  Some Common Acids and Bases and their Household Uses.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acids</strong></td>
<td></td>
</tr>
<tr>
<td>Acetic acid, CH₃COOH</td>
<td>Flavoring, preservative</td>
</tr>
<tr>
<td>Citric acid, H₃C₆H₅O₇</td>
<td>Flavoring</td>
</tr>
<tr>
<td>Ascorbic acid, H₂C₆H₆O₆</td>
<td>Vitamin C; nutritional supplement</td>
</tr>
<tr>
<td>Aluminum salts, NaAl(SO₄)₂·12H₂O</td>
<td>In baking powder, with sodium hydrogen carbonate</td>
</tr>
<tr>
<td><strong>Bases</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide (lye), NaOH</td>
<td>Oven and drain cleaners</td>
</tr>
<tr>
<td>Ammonia, NH₃</td>
<td>Household cleaner</td>
</tr>
<tr>
<td>Sodium carbonate, Na₂CO₃</td>
<td>Water softener, grease remover</td>
</tr>
<tr>
<td>Sodium hydrogen carbonate, NaHCO₃</td>
<td>Fire extinguisher, rising agent in cake mixes (baking soda), mild antacid</td>
</tr>
<tr>
<td>Sodium phosphate, Na₃PO₄</td>
<td>Cleaner for surfaces before painting or wallpapering</td>
</tr>
</tbody>
</table>
16.1 Arrhenius Acid-Base Definition

This is the earliest acid-base definition, which classifies these substances in terms of their behavior in water.

An **acid** is a substance with H in its formula that dissociates to yield $H_3O^+$. 

A **base** is a substance with OH in its formula that dissociates to yield $OH^-$. 

When an acid reacts with a base, they undergo neutralization:

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$
An acid is a **proton donor**, any species that donates an $H^+$ ion.
- An acid must contain H in its formula.

A base is a **proton acceptor**, any species that accepts an $H^+$ ion.
- A base must contain a **lone pair of electrons** to bond to $H^+$.

An acid-base reaction is a **proton-transfer process**.
Figure 16.2  Dissolving of an acid or base in water as a Brønsted-Lowry acid-base reaction.

Lone pair binds H$^+$

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

Lone pair binds H$^+$

\[ \text{NH}_3 (\text{base, H}^+\text{ acceptor}) + \text{H}_2\text{O (acid, H}^+\text{ donor)} \rightarrow \text{NH}_4^+ + \text{OH}^- \]
Conjugate Acid-Base Pairs

In the **forward** reaction:

\[
\text{NH}_3 \text{ accepts a } H^+ \text{ to form NH}_4^+. \\
H_2S + \text{NH}_3 \rightleftharpoons \text{HS}^- + \text{NH}_4^+
\]

\text{H}_2\text{S donates a } H^+ \text{ to form HS}^-.

In the **reverse** reaction:

\[
\text{NH}_4^+ \text{ donates a } H^+ \text{ to form NH}_3. \\
H_2S + \text{NH}_3 \rightleftharpoons \text{HS}^- + \text{NH}_4^+
\]

\text{HS}^- \text{ accepts a } H^+ \text{ to form H}_2\text{S}.
Conjugate Acid-Base Pairs

\[ \text{H}_2\text{S} + \text{NH}_3 \rightleftharpoons \text{HS}^- + \text{NH}_4^+ \]

\(\text{H}_2\text{S}\) and \(\text{HS}^-\) are a conjugate acid-base pair: \(\text{HS}^-\) is the conjugate base of the acid \(\text{H}_2\text{S}\).

\(\text{NH}_3\) and \(\text{NH}_4^+\) are a conjugate acid-base pair: \(\text{NH}_4^+\) is the conjugate acid of the base \(\text{NH}_3\).

A Brønsted-Lowry acid-base reaction occurs when an acid and a base react to form their conjugate base and conjugate acid, respectively.

\[ \text{acid}_1 + \text{base}_2 \rightleftharpoons \text{base}_1 + \text{acid}_2 \]
Table 16.2 The Conjugate Pairs in some Acid-Base Reactions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Acid</th>
<th>Base</th>
<th>Conjugate Pair</th>
<th>Acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction 1</td>
<td>HF</td>
<td>H₂O</td>
<td>⇌</td>
<td>F⁻</td>
</tr>
<tr>
<td>Reaction 2</td>
<td>HCOOH</td>
<td>CN⁻</td>
<td>⇌</td>
<td>HCOO⁻</td>
</tr>
<tr>
<td>Reaction 3</td>
<td>NH₄⁺</td>
<td>CO₃²⁻</td>
<td>⇌</td>
<td>NH₃</td>
</tr>
<tr>
<td>Reaction 4</td>
<td>H₂PO₄⁻</td>
<td>OH⁻</td>
<td>⇌</td>
<td>HPO₄²⁻</td>
</tr>
<tr>
<td>Reaction 5</td>
<td>H₂SO₄</td>
<td>N₂H₅⁺</td>
<td>⇌</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>Reaction 6</td>
<td>HPO₄²⁻</td>
<td>SO₃²⁻</td>
<td>⇌</td>
<td>PO₄³⁻</td>
</tr>
</tbody>
</table>

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**Sample Problem 16.1**  
Identifying Conjugate Acid-Base Pairs

**PROBLEM:** The following reactions are important environmental processes. Identify the conjugate acid-base pairs.

(a) \( \text{H}_2\text{PO}_4^- (aq) + \text{CO}_3^{2-} (aq) \rightleftharpoons \text{HPO}_4^{2-} (aq) + \text{HCO}_3^- (aq) \)

(b) \( \text{H}_2\text{O}(l) + \text{SO}_3^{2-} (aq) \rightleftharpoons \text{OH}^- (aq) + \text{HSO}_3^- (aq) \)

**PLAN:** To find the conjugate pairs, we find the species that donated an \( \text{H}^+ \) (acid) and the species that accepted it (base). The acid donates an \( \text{H}^+ \) to becomes its conjugate base, and the base accepts an \( \text{H}^+ \) to becomes it conjugate acid.

**SOLUTION:**

(a) \( \text{H}_2\text{PO}_4^- (aq) + \text{CO}_3^{2-} (aq) \rightleftharpoons \text{HPO}_4^{2-} (aq) + \text{HCO}_3^- (aq) \)

The conjugate acid-base pairs are \( \text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-} \) and \( \text{CO}_3^{2-} / \text{HCO}_3^- \).
Sample Problem 16.1

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

acid\textsubscript{1} base\textsubscript{2} base\textsubscript{1} acid\textsubscript{2}

The conjugate acid-base pairs are H\textsubscript{2}O/OH\textsuperscript{-} and SO\textsubscript{3}\textsuperscript{2-}/HSO\textsubscript{3}\textsuperscript{-}. 

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The net direction of an acid-base reaction depends on the relative strength of the acids and bases involved.

A reaction will favor the formation of the weaker acid and base.

\[
\text{H}_2\text{S} + \text{NH}_3 \rightleftharpoons \text{HS}^- + \text{NH}_4^+ 
\]

stronger acid  weaker base  stronger base  weaker acid

This reaction favors the formation of the products.
Figure 16.3 Strengths of conjugate acid-base pairs.

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>Cl⁻</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>HSO₄⁻</td>
</tr>
<tr>
<td>HNO₃</td>
<td>NO₃⁻</td>
</tr>
<tr>
<td>H₂O⁺</td>
<td>H₂O</td>
</tr>
<tr>
<td>HSO₄⁻</td>
<td>SO₄²⁻</td>
</tr>
<tr>
<td>H₂SO₃</td>
<td>HSO₃⁻</td>
</tr>
<tr>
<td>H₃PO₄</td>
<td>H₂PO₄⁻</td>
</tr>
<tr>
<td>HF</td>
<td>F⁻</td>
</tr>
<tr>
<td>CH₃COOH</td>
<td>CH₃COO⁻</td>
</tr>
<tr>
<td>H₂CO₃</td>
<td>HCO₃⁻</td>
</tr>
<tr>
<td>H₂S</td>
<td>HS⁻</td>
</tr>
<tr>
<td>HSO₃⁻</td>
<td>SO₃²⁻</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>HPO₄²⁻</td>
</tr>
<tr>
<td>HCN</td>
<td>CN⁻</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>NH₃</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>CO₃²⁻</td>
</tr>
<tr>
<td>H₂PO₄⁻</td>
<td>PO₄³⁻</td>
</tr>
<tr>
<td>H₂O</td>
<td>OH⁻</td>
</tr>
<tr>
<td>HS⁻</td>
<td>S²⁻</td>
</tr>
<tr>
<td>OH⁻</td>
<td>O²⁻</td>
</tr>
</tbody>
</table>

The stronger the acid is, the weaker its conjugate base. When an acid reacts with a base that is farther down the list, the reaction proceeds to the right ($K_c > 1$).
Sample Problem 16.2  Predicting the Net Direction of an Acid-Base Reaction

PROBLEM: Predict the net direction and whether $K$ is greater or less than 1 for each of the following reactions (assume equal initial concentrations of all species):

(a) $\text{H}_2\text{PO}_4^-(aq) + \text{NH}_3(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{NH}_4^+(aq)$

(b) $\text{H}_2\text{O(l)} + \text{HS}^-(aq) \rightleftharpoons \text{OH}^-(aq) + \text{H}_2\text{S}(aq)$

PLAN: We identify the conjugate acid-base pairs and consult figure 18.8 to see which acid and base are stronger. The reaction favors the formation of the weaker acid and base.

SOLUTION:

(a) $\text{H}_2\text{PO}_4^-(aq) + \text{NH}_3(aq) \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{NH}_4^+(aq)$

<table>
<thead>
<tr>
<th>stronger acid</th>
<th>stronger base</th>
<th>weaker base</th>
<th>weaker acid</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{PO}_4^-$</td>
<td>$\text{NH}_3$</td>
<td>$\text{HPO}_4^{2-}$</td>
<td>$\text{NH}_4^+$</td>
</tr>
</tbody>
</table>

The net direction for this reaction is to the right, so $K > 1$. ©2013 McGraw-Hill Ryerson Limited
Sample Problem 16.2

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

*weaker acid  weaker base  stronger base  stronger acid*

The net direction for this reaction is to the left, so \( K < 1 \).
Sample Problem 16.3  Using Molecular Scenes to Predict the Net Direction of an Acid-Base Reaction

PROBLEM:  Given that 0.10 \( M \) of HX (blue and green) has a pH of 2.88, and 0.10 \( M \) HY (blue and orange) has a pH 3.52, which scene best represents the final mixture after equimolar solutions of HX and Y\(^-\) are mixed?

PLAN:  A stronger acid and base yield a weaker acid and base, so we have to determine the relative acid strengths of HX and HY to choose the correct molecular scene. The concentrations of the acid solutions are equal, so we can recognize the stronger acid by comparing the pH values of the two solutions.
Sample Problem 16.3

SOLUTION:

The HX solution has a lower pH than the HY solution, so HX is the stronger acid and Y\(^-\) is the stronger base. The reaction of HX and Y\(^-\) has a $K_c > 1$, which means the equilibrium mixture will contain more HY than HX.

Scene 1 has equal numbers of HX and HY, which could occur if the acids were of equal strength. Scene 2 shows fewer HY than HX, which would occur if HY were the stronger acid.

**Scene 3 is consistent with the relative acid strengths, because it contains more HY than HX.**
Strong and Weak Acids

A **strong** acid dissociates **completely** into ions in water:

\[
HA(g \text{ or } l) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq)
\]

A dilute solution of a **strong** acid contains **no HA molecules**.

A **weak** acid dissociates **slightly** to form ions in water:

\[
HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)
\]

In a dilute solution of a **weak** acid, **most HA molecules are undissociated**.

\[
K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \text{has a very small value.}
\]
Strong acid: \( HA(g \text{ or } l) + H_2O(l) \rightarrow H_3O^+(aq) + A^-(aq) \)

There are no HA molecules in solution.
Figure 16.4B  The extent of dissociation for weak acids.

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

Most HA molecules are undissociated.
The Acid Dissociation Constant, $K_a$

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

OR

$$\text{HA}(aq) \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq)$$

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

The value of $K_a$ is an indication of acid strength.

Stronger acid $\rightarrow$ higher $[\text{H}_3\text{O}^+]$ $\rightarrow$ larger $K_a$

Weaker acid $\rightarrow$ lower % dissociation of HA $\rightarrow$ smaller $K_a$
### Table 16.4  \( K_a \) Values for some Monoprotic Acids at 25°C

<table>
<thead>
<tr>
<th>Name (Formula)</th>
<th>Lewis Structure*</th>
<th>( K_a )</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorous acid (HClO₂)</td>
<td>( \text{H} - \text{O} - \text{Cl} - \text{O} )</td>
<td>( 1.1 \times 10^{-2} )</td>
<td>1.96</td>
</tr>
<tr>
<td>Nitrous acid (HNO₂)</td>
<td>( \text{H} - \text{O} - \text{N} = \text{O} )</td>
<td>( 7.1 \times 10^{-4} )</td>
<td>3.15</td>
</tr>
<tr>
<td>Hydrofluoric acid (HF)</td>
<td>( \text{H} - \text{F}^- )</td>
<td>( 6.8 \times 10^{-4} )</td>
<td>3.17</td>
</tr>
<tr>
<td>Formic acid (HCOOH)</td>
<td>( \text{H} - \text{C} - \text{O}^- \text{H} )</td>
<td>( 1.8 \times 10^{-4} )</td>
<td>3.74</td>
</tr>
<tr>
<td>Acetic acid (CH₃COOH)</td>
<td>( \text{H} - \text{C} - \text{C} - \text{O}^- \text{H} )</td>
<td>( 1.8 \times 10^{-5} )</td>
<td>4.74</td>
</tr>
<tr>
<td>Propanoic acid (CH₃CH₂COOH)</td>
<td>( \text{H} - \text{C} - \text{C} - \text{C} - \text{O}^- \text{H} )</td>
<td>( 1.3 \times 10^{-5} )</td>
<td>4.89</td>
</tr>
<tr>
<td>Hypochlorous acid (HClO)</td>
<td>( \text{H} - \text{O} - \text{Cl}^- )</td>
<td>( 2.9 \times 10^{-8} )</td>
<td>7.54</td>
</tr>
<tr>
<td>Hydrocyanic acid (HCN)</td>
<td>( \text{H} - \text{C} \equiv \text{N}^- )</td>
<td>( 6.2 \times 10^{-10} )</td>
<td>9.21</td>
</tr>
</tbody>
</table>

*Red type indicates the ionizable proton; all atoms have zero formal charge.*
Classifying the Relative Strengths of Acids

• **Strong acids** include
  – the hydrohalic acids (HCl, HBr, and HI) and
  – oxoacids in which the number of O atoms exceeds the number of ionizable protons by two or more (e.g., HNO₃, H₂SO₄, HClO₄.)

• **Weak acids** include
  – the hydrohalic acid HF,
  – acids in which H is not bonded to O or to a halogen (e.g., HCN),
  – oxoacids in which the number of O atoms equals or exceeds the number of ionizable protons by one (e.g., HClO, HNO₂), and
  – carboxylic acids, which have the general formula RCOOH (e.g., CH₃COOH and C₆H₅COOH.)
Classifying the Relative Strengths of Bases

• **Strong bases** include
  – water-soluble compounds containing $O^{2-}$ or $OH^{-}$ ions.
  – The cations are usually those of the most active metals:
    • $M_2O$ or $MOH$, where $M =$ Group 1 metal (Li, Na, K, Rb, Cs)
    • $MO$ or $M(OH)_2$ where $M =$ group 2 metal (Ca, Sr, Ba).

• **Weak bases** include
  – ammonia ($NH_3$),
  – amines, which have the general formula $R\tilde{N}H_2$, $R_2\tilde{N}H$, or $R_3\tilde{N}$
  – The common structural feature is an N atom with a lone electron pair.
Water dissociates very slightly into ions in an equilibrium process known as *autoionization* or *self-ionization*.

\[
H_2O \ (l) \rightleftharpoons H^+ \ (aq) + OH^- \ (aq)
\]
The Ion-Product Constant for Water ($K_w$)

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

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ (at 25°C)}$$

In pure water,

$$[H^+] = [OH^-] = \boxed{1.0 \times 10^{-7}} \text{ (at 25°C)}$$

Both ions are present in all aqueous systems.
A change in \([H_3O^+]\) causes an inverse change in \([OH^-]\), and vice versa.

- Higher \([H^+]\) \(\rightarrow\) lower \([OH^-]\)
- Higher \([OH^-]\) \(\rightarrow\) lower \([H^+]\)

We can define the terms “acidic” and “basic” in terms of the relative concentrations of \(H_3O^+\) and \(OH^-\) ions:

<table>
<thead>
<tr>
<th>Condition</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>In an acidic solution,</td>
<td>([H^+] &gt; [OH^-])</td>
</tr>
<tr>
<td>In a neutral solution,</td>
<td>([H^+] = [OH^-])</td>
</tr>
<tr>
<td>In basic solution,</td>
<td>([H^+] &lt; [OH^-])</td>
</tr>
</tbody>
</table>

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Figure 16.6  The relationship between $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ and the relative acidity of solutions.

[Diagram showing the relationship between $[\text{H}^+]$ and $[\text{OH}^-]$ and the acidity of solutions.]

$[\text{H}^+] > [\text{OH}^-]$: Acidic solution

$[\text{H}^+] = [\text{OH}^-]$: Neutral solution

$[\text{H}^+] < [\text{OH}^-]$: Basic solution

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Sample Problem 16.5  Calculating $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ in an Aqueous Solution

PROBLEM: A research chemist adds a measured amount of HCl gas to pure water at 25°C and obtains a solution with $[\text{H}_3\text{O}^+] = 3.0 \times 10^{-4} \text{ M}$. Calculate $[\text{OH}^-]$. Is the solution neutral, acidic, or basic?

PLAN: We use the known value of $K_w$ at 25°C (1.0$\times$10$^{-14}$) and the given $[\text{H}^+]$ to solve for $[\text{OH}^-]$. We can then compare $[\text{H}_3\text{O}^+]$ with $[\text{OH}^-]$ to determine whether the solution is acidic, basic, or neutral.

SOLUTION:

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

$[\text{OH}^-] = \frac{K_w}{[\text{H}^+]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-4}} = 3.3 \times 10^{-11} \text{ M}$

$[\text{H}^+]$ is $> [\text{OH}^-]$ and the solution is acidic.
The pH Scale

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

The pH of a solution indicates its relative acidity:

- In an acidic solution, \( \text{pH} < 7.00 \)
- In a neutral solution, \( \text{pH} = 7.00 \)
- In basic solution, \( \text{pH} > 7.00 \)

The \textit{higher} the pH, the \textit{lower} the \([H^+]\) and the \textit{less acidic} the solution.
pH, pOH, and p$K_w$

$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 25°C

\[
pH = -\log[H^+]
\]
\[
pOH = -\log[OH^-]
\]

$pK_w = pH + pOH = 14.00$ at 25°C

$pH + pOH = pK_w$ for any aqueous solution at any temperature.

Since $K_w$ is a constant, the values of pH, pOH, [H$^+$], and [OH$^-$] are interrelated:

- If [H$^+$] increases, [OH$^-$] decreases (and vice versa).
- If pH increases, pOH decreases (and vice versa).
Figure 16.8  The relations among $[\text{H}_3\text{O}^+]$, pH, $[\text{OH}^-]$, and pOH.

<table>
<thead>
<tr>
<th>$[\text{H}_3\text{O}^+]$</th>
<th>pH</th>
<th>$[\text{OH}^-]$</th>
<th>pOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1.0 \times 10^{-15}$</td>
<td>15.00</td>
<td>$1.0 \times 10^1$</td>
<td>-1.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-14}$</td>
<td>14.00</td>
<td>$1.0 \times 10^0$</td>
<td>0.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-13}$</td>
<td>13.00</td>
<td>$1.0 \times 10^{-1}$</td>
<td>1.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-12}$</td>
<td>12.00</td>
<td>$1.0 \times 10^{-2}$</td>
<td>2.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-11}$</td>
<td>11.00</td>
<td>$1.0 \times 10^{-3}$</td>
<td>3.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
<td>$1.0 \times 10^{-4}$</td>
<td>4.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-9}$</td>
<td>9.00</td>
<td>$1.0 \times 10^{-5}$</td>
<td>5.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-8}$</td>
<td>8.00</td>
<td>$1.0 \times 10^{-6}$</td>
<td>6.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-7}$</td>
<td>7.00</td>
<td>$1.0 \times 10^{-7}$</td>
<td>7.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-6}$</td>
<td>6.00</td>
<td>$1.0 \times 10^{-8}$</td>
<td>8.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-5}$</td>
<td>5.00</td>
<td>$1.0 \times 10^{-9}$</td>
<td>9.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-4}$</td>
<td>4.00</td>
<td>$1.0 \times 10^{-10}$</td>
<td>10.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-3}$</td>
<td>3.00</td>
<td>$1.0 \times 10^{-11}$</td>
<td>11.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-2}$</td>
<td>2.00</td>
<td>$1.0 \times 10^{-12}$</td>
<td>12.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{-1}$</td>
<td>1.00</td>
<td>$1.0 \times 10^{-13}$</td>
<td>13.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{0}$</td>
<td>0.00</td>
<td>$1.0 \times 10^{-14}$</td>
<td>14.00</td>
</tr>
<tr>
<td>$1.0 \times 10^{1}$</td>
<td>-1.00</td>
<td>$1.0 \times 10^{-15}$</td>
<td>15.00</td>
</tr>
</tbody>
</table>

MORE BASIC

MORE ACIDIC

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PROBLEM: In an art restoration project, a conservator prepares copper-plate etching solutions by diluting concentrated HNO₃ to 2.0 mol/L, 0.30 mol/L, and 0.0063 mol/L HNO₃. Calculate [H⁺], pH, [OH⁻], and pOH of the three solutions at 25°C.

PLAN: HNO₃ is a strong acid so it dissociates completely, and [H⁺] = [HNO₃]_{init}. We use the given concentrations and the value of $K_w$ at 25°C to find [H⁺] and [OH⁻]. We can then calculate pH and pOH.

SOLUTION:
Calculating the values for 2.0 mol/L HNO₃:

\[
[H^+] = 2.0 \text{ M} \quad \text{pH} = -\log[H_3O^+] = -\log(2.0) = -0.30
\]

\[
\text{[OH}^-] = \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{2.0} = 5.0 \times 10^{-15} \text{ mol/L}
\]

\[
pOH = -\log[OH^-] = -\log(5.0 \times 10^{-15}) = 14.30
\]
Sample Problem 16.6

Calculating the values for 0.30 mol/L HNO₃:

\[ [H^+] = 0.30 \text{ M} \quad \text{pH} = -\log[H^+] = -\log(0.30) = 0.52 \]

\[
\begin{align*}
[OH^-] &= \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.30} = 3.3 \times 10^{-14} \text{ mol/L} \\
pOH &= -\log[OH^-] = -\log(3.3 \times 10^{-14}) = 13.48
\end{align*}
\]

Calculating the values for 0.0063 mol/L HNO₃:

\[ [H_3O^+] = 0.0063 \text{ mol/L} \quad \text{pH} = -\log[H^+] = -\log(0.30) = 2.20 \]

\[
\begin{align*}
[OH^-] &= \frac{K_w}{[H^+]} = \frac{1.0 \times 10^{-14}}{0.0063} = 1.6 \times 10^{-12} \text{ mol/L} \\
pOH &= -\log[OH^-] = -\log(1.6 \times 10^{-12}) = 11.80
\end{align*}
\]
Figure 16.9  Methods for measuring the pH of an aqueous solution.

pH paper

pH meter

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Weak Bases

A Brønsted-Lowry base is a species that accepts an $\text{H}^+$. For a weak base that dissolves in water:

$$\text{B}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{BH}^+(aq) + \text{OH}^-(aq)$$

The *base-dissociation* or *base-ionization constant* is given by:

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

Note that *no base actually dissociates* in solution, but *ions* are produced when the base reacts with $\text{H}_2\text{O}$. 
Figure 16.10 Abstraction of a proton from water by the base methylamine.

Lone pair of N pair binds $H^+$

$\text{CH}_3\text{NH}_2$ methylamine $\quad + \quad \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{CH}_3\text{NH}_3^+$ methylammonium ion $\quad + \quad \text{OH}^-$
### Table 16.6  $K_b$ Values for Some Molecular (Amine) Bases at 25°C

<table>
<thead>
<tr>
<th>Name (Formula)</th>
<th>Lewis Structure*</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diethylamine [(CH₃CH₂)₂NH]</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>8.6×10⁻⁴</td>
</tr>
<tr>
<td>Dimethylamine [(CH₃)₂NH]</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>5.9×10⁻⁴</td>
</tr>
<tr>
<td>Methylamine (CH₃NH₂)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>4.4×10⁻⁴</td>
</tr>
<tr>
<td>Ammonia (NH₃)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>1.76×10⁻⁵</td>
</tr>
<tr>
<td>Pyridine (C₅H₅N)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>1.7×10⁻⁹</td>
</tr>
<tr>
<td>Aniline (C₆H₅NH₂)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>4.0×10⁻¹⁰</td>
</tr>
</tbody>
</table>

*Blue type indicates the basic nitrogen and its lone pair.*
Anions of Weak Acids as Weak Bases

The **anions** of weak acids often function as **weak bases**.

\[
A^- (aq) + H_2O(l) \rightleftharpoons HA(aq) + OH^-(aq) \quad K_b = \frac{[HA][OH^-]}{[A^-]}
\]

A solution of HA is **acidic**, while a solution of A\(^-\) is **basic**.

HF\((aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + F^- (aq)\)

HF is a weak acid, so this equilibrium lies to the left. 
\([HF] >> [F^-]\), and \([H_3O^+]\) from HF >> \([OH^-]\) from H\(_2\)O ; 
the solution is therefore **acidic**.
If NaF is dissolved in H$_2$O, it dissolves completely, and F$^-$ can act as a weak base:

$$\text{F}^- (aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HF}(aq) + \text{OH}^-(aq)$$

HF is a weak acid, so this equilibrium also lies to the left. [F$^-$] $\gg$ [HF], and [OH$^-$] from F$^-$ $\gg$ [H$_3$O$^+$] from H$_2$O; the solution is therefore basic.
**Ka and Kb for a Conjugate Acid-Base Pair**

\[
\begin{align*}
\text{HA} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^- \\
\text{A}^- + \text{H}_2\text{O} & \rightleftharpoons \text{HA} + \text{OH}^- \\
2\text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-
\end{align*}
\]

\(K_c\) for the overall equation = \(K_1 \times K_2\), so

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

\(K_a \times K_b = K_w\)

This relationship is true for any conjugate acid-base pair.
Solving Problems Involving Weak-Acid/Base Equilibria

The notation system

• Molar concentrations are indicated by [ ].
• A bracketed formula with no subscript indicates an equilibrium concentration.

The assumptions

• \([\text{H}_3\text{O}^+]\) from the autoionization of \(\text{H}_2\text{O}\) is negligible.
• A weak acid has a small \(K_a\) and its dissociation is negligible. \([\text{HA}] \approx [\text{HA}]_{\text{init}}\).
• OR for weak bases, \([\text{B}] \approx [\text{B}]_{\text{init}}\).
**Sample Problem 16.7**  

**Finding $K_a$ of a Weak Acid from the Solution pH**

**PROBLEM:** A substance called 2-phenylacetic acid ($C_6H_5CH_2COOH$, simplified here as HPAc) builds up in the blood of persons with phenylketonuria, an inherited disorder that, if untreated, causes mental retardation and death. A study of the acid shows that the pH of 0.12 mol/L HPAc is 2.62. What is the $K_a$ of phenylacetic acid?

**PLAN:** We start with the balanced dissociation equation and write the expression for $K_a$. We assume that $[H_3O^+]$ from $H_2$ is negligible and use the given pH to find $[H_3O^+]$, which equals $[PAc^-]$ and $[HPAc]_{dissoc}$. We assume that $[HPAc] \approx [HPAc]_{init}$ because HPAc is a weak acid.

**SOLUTION:**

$$HPAc(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + PAc^-(aq)$$

$$K_a = \frac{[H_3O^+][PAc^-]}{[HPAc]}$$
Sample Problem 16.7

<table>
<thead>
<tr>
<th>Concentration (mol/L)</th>
<th>HPAc(aq)</th>
<th>H₂O(l)</th>
<th>H₃O⁺(aq)</th>
<th>PAc⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.12</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.12 - x</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ [H₃O⁺] = 10^{-pH} = 2.4 \times 10^{-3} \text{ mol/L} \] which is >> 10⁻⁷ (the [H₃O⁺] from water)

\[ x \approx 2.4 \times 10^{-3} M \approx [H₃O⁺] \approx [PAc⁻] \]

[HPAc] = 0.12 - x ≈ 0.12 mol/L

So \( K_a = \frac{(2.4 \times 10^{-3}) (2.4 \times 10^{-3})}{0.12} = 4.8 \times 10^{-5} \)

Checking the assumptions by finding the percent error in concentration:

\[ [H₃O⁺]_{from H₂O} = \frac{1 \times 10^{-7} \text{ mol/L}}{2.4 \times 10^{-3} \text{ mol/L}} \times 100 = 4 \times 10^{-3} \% (<5\%; assumption is justified). \]

\[ [HPAc]_{dissoc} = \frac{2.4 \times 10^{-3} \text{ mol/L}}{0.12 \text{ mol/L}} \times 100 = 2.0 \% (<5\%; assumption is justified). \]

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Sample Problem 16.8  Determining Concentration from $K_a$ and Initial [HA]

**PROBLEM:** Propanoic acid (CH$_3$CH$_2$COOH, which we simplify as EtCOOH) is a carboxylic acid whose salts are used to retard mold growth in foods. What is the [H$_3$O$^+$] of 0.10 mol/L EtCOOH ($K_a = 1.3 \times 10^{-5}$)?

**PLAN:** We write a balanced equation and the expression for $K_a$. We know [EtCOOH]$_{init}$ but not [EtCOOH] (i.e., the concentration at equilibrium). We define $x$ as [EtCOOH]$_{dissoc}$ and set up a reaction table. We assume that, since EtCOOH has a small $K_a$ value, it dissociates very little and therefore [EtCOOH] $\approx$ [EtCOOH]$_{init}$.

**SOLUTION:**

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

\[
K_a = \frac{[\text{H}_3\text{O}^+][\text{EtCOO}^-]}{[\text{EtCOOH}]}
\]
Sample Problem 16.8

Concentration (M) EtCOOH(aq) + H₂O(l) ⇄ H₃O⁺(aq) + EtCOO⁻

<table>
<thead>
<tr>
<th></th>
<th>Initial</th>
<th>Change</th>
<th>Equilibrium</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtCOOH(aq)</td>
<td>0.10</td>
<td>-</td>
<td>0.10 - x</td>
</tr>
<tr>
<td>H₂O(l)</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>H₃O⁺(aq)</td>
<td>0</td>
<td>+x</td>
<td>x</td>
</tr>
<tr>
<td>EtCOO⁻(aq)</td>
<td>0</td>
<td></td>
<td>x</td>
</tr>
</tbody>
</table>

Since $K_a$ is small, we will assume that $x << 0.10$ and $[\text{EtCOOH}] \approx 0.10 \text{ mol/L}$.

$$K_a = 1.3 \times 10^{-5} = \frac{\text{[H}_3\text{O}^+\text{][EtCOO}^\text{⁻}]}{\text{[EtCOOH]}} = \frac{x^2}{0.10}$$

$$x = \sqrt{(0.10)(1.3 \times 10^{-5})} = 1.1 \times 10^{-3} \text{ mol/L} = [\text{H}_3\text{O}^+]$$

Check: $[\text{EtCOOH}]_{\text{diss}} = \frac{1.1 \times 10^{-3} \text{ mol/L}}{0.10 \text{ mol/L}} \times 100 = 1.1\%$ (< 5%; assumption is justified.)
Sample Problem 16.9  Determining pH from $K_b$ and Initial [B]

**PROBLEM:** Dimethylamine, $(CH_3)_2NH$, a key intermediate in detergent manufacture, has a $K_b$ of $5.9 \times 10^{-4}$. What is the pH of 1.5 mol/L $(CH_3)_2NH$?

**PLAN:** We start with the balanced equation for the reaction of the amine with $H_2O$, remembering that it is a weak base. We then write the expression for $K_b$, set up a reaction table and solve for $[OH^-]$. From $[OH^-]$ we can calculate $[H_3O^+]$ and pH. We make similar assumptions to those made for weak acids. Since $K_b \gg K_w$, the $[OH^-]$ from $H_2O$ is negligible. Since $K_b$ is small, we can assume that the amount of amine reacting is also small, so $[(CH_3)_2NH] \approx [(CH_3)_2NH]_{init}$.

**SOLUTION:**

$$\begin{align*}
(CH_3)_2NH(aq) + H_2O(l) & \rightleftharpoons (CH_3)_2NH_2^+(aq) + OH^- (aq) \\
K_b &= \frac{[(CH_3)_2NH_2^+][OH^-]}{[(CH_3)_2NH]} \\
\end{align*}$$
Sample Problem 16.9

\[
\begin{array}{lccccc}
\text{Concentration (mol/L)} & (\text{CH}_3)_2\text{NH}(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons & (\text{CH}_3)_2\text{NH}_2^+(aq) + \text{OH}^-(aq) \\
\text{Initial} & 1.50 & - & 0 & 0 \\
\text{Change} & -x & - & +x & +x \\
\text{Equilibrium} & 1.50 - x & - & x & x \\
\end{array}
\]

Since \( K_b \) is small, \( x \ll 1.50 \) and \( 1.50 - x \approx 1.50 \)

\[
K_b = \frac{[(\text{CH}_3)_2\text{NH}_2^+][\text{OH}^-]}{[(\text{CH}_3)_2\text{NH}]} = 5.9 \times 10^{-4} \approx \frac{x^2}{1.5}
\]

\( x = [\text{OH}^-] = 3.0 \times 10^{-2} \text{ mol/L} \)

Check assumption:

\[
\frac{3.0 \times 10^{-2} \text{ mol/L}}{1.5 \text{ mol/L}} \times 100 = 2.0\% (\text{< 5\%; assumption is justified})
\]
Sample Problem 16.9

\[
[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-2}} = 3.3 \times 10^{-13} \text{ mol/L}
\]

\[\text{pH} = -\log (3.3 \times 10^{-13}) = 12.48\]
Sample Problem 16.11  Determining the pH of a Solution of A⁻

PROBLEM: Sodium acetate (CH₃COONa, or NaOAc for this problem) has applications in photographic development and textile dyeing. What is the pH of 0.25 mol/L NaOAc? $K_a$ of acetic acid (HAc) is $1.8 \times 10^{-5}$.

PLAN: Sodium salts are soluble in water and acetate is the anion of HAc so it acts as a weak base. We write the base dissociation equation and the expression for $K_b$, and solve for [OH⁻]. We recall that any soluble ionic salt dissociates completely in solution, so $[OAc^-]_{init} = 0.25$ mol/L.

SOLUTION: $OAc^- (aq) + H_2O(l) \rightleftharpoons HOAc(aq) + OH^-(aq)$

$$K_b = \frac{[HAc][OH^-]}{[OAc^-]}$$

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Sample Problem 16.11

<table>
<thead>
<tr>
<th>Concentration (mol/L)</th>
<th>OAc⁻(aq)</th>
<th>H₂O(l)</th>
<th>HOAc(aq)</th>
<th>OH⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.25</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Change</td>
<td>-x</td>
<td>-</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>0.25 - x</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \text{ mol/L} \]

\[ K_b = 5.6 \times 10^{-10} = \frac{[\text{HOAc}][\text{OH}^-]}{[\text{OAc}^-]} \approx \frac{x^2}{0.25} \]

so \( x = [\text{OH}^-] = 1.2 \times 10^{-5} \text{ mol/L} \)

Checking the assumption:

OK!
Sample Problem 16.11

\[
[H_3O^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{1.2 \times 10^{-5}} = 8.3 \times 10^{-10} \text{ mol/L}
\]

\[
pH = -\log (8.3 \times 10^{-10}) = 9.08
\]
A *polyprotic acid* is an acid with more than one ionizable proton. In solution, each dissociation step has a different value for $K_a$:

\[
\begin{align*}
\text{H}_3\text{PO}_4(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{H}_2\text{PO}_4^-(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a1} = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{H}_2\text{PO}_4^-\right]}{\left[\text{H}_3\text{PO}_4\right]} = 7.2 \times 10^{-3} \\
\text{H}_2\text{PO}_4^-(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{HPO}_4^{2-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a2} = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{HPO}_4^{2-}\right]}{\left[\text{H}_2\text{PO}_4^-\right]} = 6.3 \times 10^{-8} \\
\text{HPO}_4^{2-}(aq) + \text{H}_2\text{O}(l) & \rightleftharpoons \text{PO}_4^{3-}(aq) + \text{H}_3\text{O}^+(aq) \quad K_{a3} = \frac{\left[\text{H}_3\text{O}^+\right]\left[\text{PO}_4^{3-}\right]}{\left[\text{HPO}_4^{2-}\right]} = 4.2 \times 10^{-13}
\end{align*}
\]

$K_{a1} > K_{a2} > K_{a3}$

We usually neglect $\left[\text{H}_3\text{O}^+\right]$ produced after the first dissociation.
Table 16.7  Successive $K_a$ values for Some Polyprotic Acids at 25°C

<table>
<thead>
<tr>
<th>Name (Formula)</th>
<th>Lewis Structure*</th>
<th>$K_{a1}$</th>
<th>$K_{a2}$</th>
<th>$K_{a3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxalic acid ($H_2C_2O_4$)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>$5.6 \times 10^{-2}$</td>
<td>$5.4 \times 10^{-5}$</td>
<td></td>
</tr>
<tr>
<td>Sulfurous acid ($H_2SO_3$)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>$1.4 \times 10^{-2}$</td>
<td>$6.5 \times 10^{-8}$</td>
<td></td>
</tr>
<tr>
<td>Phosphoric acid ($H_3PO_4$)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>$7.2 \times 10^{-3}$</td>
<td>$6.3 \times 10^{-8}$</td>
<td>$4.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>Arsenic acid ($H_3AsO_4$)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>$6 \times 10^{-3}$</td>
<td>$1.1 \times 10^{-7}$</td>
<td>$3 \times 10^{-12}$</td>
</tr>
<tr>
<td>Carbonic acid ($H_2CO_3$)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>$4.5 \times 10^{-7}$</td>
<td>$4.7 \times 10^{-11}$</td>
<td></td>
</tr>
<tr>
<td>Hydrosulfuric acid ($H_2S$)</td>
<td><img src="image" alt="Lewis Structure" /></td>
<td>$9 \times 10^{-8}$</td>
<td>$1 \times 10^{-17}$</td>
<td></td>
</tr>
</tbody>
</table>

*Red type indicates the ionizable protons.
Sample Problem 16.12  Calculating Equilibrium Concentrations for a Polyprotic Acid

**PROBLEM:** Ascorbic acid (H$_2$C$_6$H$_6$O$_6$; H$_2$Asc for this problem), known as vitamin C, is a diprotic acid ($K_{a1} = 1.0 \times 10^{-5}$ and $K_{a2} = 5 \times 10^{-12}$) found in citrus fruit. Calculate [H$_2$Asc], [HAsc$^-$], [Asc$^{2-}$], and the pH of 0.050 mol/L H$_2$Asc.

**PLAN:** We first write the dissociation equations and the associated $K_a$ expressions. Since $K_{a1} >> K_{a2}$, we can assume that the first dissociation produces almost all the H$_3$O$^+$. Also, since $K_{a1}$ is small, the amount of H$_2$ASC that dissociates can be neglected. We set up a reaction table for the first dissociation, with $x$ equal to [H$_2$Asc]$_{dissoc}$, and solve for [H$_3$O$^+$] and [HAsc$^-$].

**SOLUTION:**

\[
\begin{align*}
H_2\text{Asc}(aq) + H_2O(l) & \rightleftharpoons H\text{Asc}^-(aq) + H_3O^+(aq) \quad K_{a1} = \frac{[H\text{Asc}^-][H_3O^+]}{[H_2\text{Asc}]} = 1.0 \times 10^{-5} \\
H\text{Asc}^-(aq) + H_2O(l) & \rightleftharpoons \text{Asc}^{2-}(aq) + H_3O^+(aq) \quad K_{a2} = \frac{[\text{Asc}^{2-}][H_3O^+]}{[H\text{Asc}^-]} = 5 \times 10^{-12}
\end{align*}
\]
Sample Problem 16.12

**Concentration (mol/L)**

<table>
<thead>
<tr>
<th></th>
<th>$\text{H}_2\text{Asc}(aq)$</th>
<th>$\text{H}_2\text{O}(l)$</th>
<th>$\rightleftharpoons$</th>
<th>$\text{HAsc}^-(aq)$</th>
<th>$\text{H}_3\text{O}^+(aq)$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial</strong></td>
<td>0.050</td>
<td>-</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td><strong>Change</strong></td>
<td>$-x$</td>
<td>-</td>
<td>$+x$</td>
<td>$+x$</td>
<td></td>
</tr>
<tr>
<td><strong>Equilibrium</strong></td>
<td>0.050 - $x$</td>
<td>-</td>
<td>$x$</td>
<td>$x$</td>
<td></td>
</tr>
</tbody>
</table>

$$K_{a1} = \frac{[\text{HAsc}^-][\text{H}_3\text{O}^+]}{[\text{H}_2\text{Asc}]} = 1.0 \times 10^{-5} = \frac{x^2}{0.050 - x} \approx \frac{x^2}{0.050}$$

$$x = [\text{H}_3\text{O}^+] = [\text{HAsc}^-] = \sqrt{(0.050)(1.0 \times 10^{-5})} = 7.1 \times 10^{-4} \text{ mol/L}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(7.1 \times 10^{-4}) = 3.15$$
Sample Problem 16.12

Checking assumptions:

1. \([\text{H}_3\text{O}^+]_{\text{from HAsc}^-} \ll [\text{H}_3\text{O}^+]_{\text{from H}_2\text{Asc}}\) : For any second dissociation,

\[
[\text{H}_3\text{O}^+]_{\text{from HAsc}^-} \approx \frac{[\text{HAsc}^-](K_{a2})}{0.050} = \frac{(7.1 \times 10^{-4})(5 \times 10^{-12})}{0.050} = 6 \times 10^{-8} \text{ mol/L}
\]

This is even less than \([\text{H}_3\text{O}^+]_{\text{from H}_2\text{O}}\), so the assumption is justified.

2. \([\text{H}_2\text{Asc}]_{\text{dissoc}} \ll [\text{H}_2\text{Asc}]_{\text{init}}\):

\[
\frac{7.1 \times 10^{-4} \text{ M}}{0.050 \text{ M}} \times 100 = 1.4\% (< 5\%; \text{ assumption is justified})
\]
Acid Strength of Nonmetal Hydrides

For nonmetal hydrides (E-H), acid strength depends on:

- the electronegativity of the central nonmetal (E), and
- the strength of the E-H bond.

**Across** a period, acid strength *increases*.
Electronegativity increases across a period, so the acidity of E-H increases.

**Down** a group, acid strength *increases*.
The length of the E-H bond increases down a group and its bond strength therefore decreases.
Figure 16.11  The effect of atomic and molecular properties on nonmetal hydride acidity.
Acid Strength of Oxoacids

All oxoacids have the acidic H bonded to an O atom.

Acid strength of oxoacids depends on:
• the electronegativity of the central nonmetal (E), and
• the number of O atoms around E.

For oxoacids with the same number of O atoms, acid strength increases as the electronegativity of E increases.

For oxoacids with different numbers of O atoms, acid strength increases with the number of O atoms.
Figure 16.12 The relative strengths of oxoacids.

A

\[
\begin{align*}
& \text{Electronegativity increases, so acidity increases.} \\
& \text{H} - \text{O} - \text{I} < \text{H} - \text{O} - \text{Br} < \text{H} - \text{O} - \text{Cl} \\
& \text{?}^+ \text{?}^- \quad \text{?}^+ \text{?}^- \quad \text{?}^+ \text{?}^-
\end{align*}
\]

B

\[
\begin{align*}
& \text{Number of O atoms increases, so acidity increases.} \\
& \text{H} - \text{O} - \text{Cl} < \text{H} - \text{O} - \text{Cl} \quad \text{Cl} = \text{O} \\
& \text{?}^+ \text{?}^- \quad \text{?}^+ \text{?}^- \quad \text{?}^+ \text{?}^-
\end{align*}
\]

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Some **hydrated** metal ions are able to transfer an $\text{H}^+$ to $\text{H}_2\text{O}$. These metal ions will form **acidic** solutions.

Consider a metal ion in solution, $\text{M}^{n+}$:

$$\text{M}^{n+}(aq) + \text{H}_2\text{O}(l) \rightarrow \text{M(H}_2\text{O)}_x^{n+}(aq)$$

If $\text{M}^{n+}$ is **small** and **highly charged**, it will withdraw enough $\text{e}^-$ density from the O-H bonds of the bound $\text{H}_2\text{O}$ molecules to release $\text{H}^+$:

$$\text{M(H}_2\text{O)}_x^{n+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{M(H}_2\text{O)}_{x-1}\text{OH}^{(n-1)}(aq) + \text{H}_3\text{O}^+(aq)$$
Figure 16.13  The acidic behavior of the hydrated Al$^{3+}$ ion.

Electron density is drawn toward Al$^{3+}$. Nearby H$_2$O acts as a base. O—H bond becomes more polar.
Salts that Yield Neutral Solutions

A salt that consists of the \textit{anion} of a \textit{strong acid} and the \textit{cation} of a \textit{strong base} yields a \textit{neutral} solution.

\begin{align*}
\text{NaNO}_3 \\
\text{Na}^+ \text{ is the cation of NaOH, a strong base.} & \quad \text{NO}_3^- \text{ is the anion of HNO}_3, \text{ a strong acid.}
\end{align*}

This solution will be neutral, because neither \text{Na}^+ \text{ nor NO}_3^- \text{ will react with H}_2\text{O to any great extent.}
A salt that consists of the anion of a strong acid and the cation of a weak base yields an acidic solution.

\[
\text{NH}_4\text{Cl}
\]

\[
\text{NH}_4^+ \text{ is the cation of NH}_3, \text{ a weak base.}
\]

\[
\text{Cl}^- \text{ is the anion of HCl, a strong acid.}
\]

This solution will be acidic, because \(\text{NH}_4^+\) will react with \(\text{H}_2\text{O}\) to produce \(\text{H}_3\text{O}^+\):

\[
\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(aq) + \text{H}_3\text{O}^+(aq)
\]
A salt that consists of the anion of a weak acid and the cation of a strong base yields a basic solution.

\[ \text{CH}_3\text{COONa} \]

CH\(_3\)COO\(^-\) is the anion of CH\(_3\)COOH, a weak acid. Na\(^+\) is the cation of NaOH, a strong base.

This solution will be basic, because CH\(_3\)COO\(^-\) will react with H\(_2\)O to produce OH\(^-\):

\[ \text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l) \leftrightharpoons \text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \]
Sample Problem 16.13  Predicting Relative Acidity of Salt Solutions from Reactions of the Ions with Water

PROBLEM: Predict whether aqueous solutions of the following are acidic, basic, or neutral, and write an equation for the reaction of any ion with water:

(a) Potassium perchlorate, $\text{KClO}_4$   (b) Sodium benzoate, $\text{C}_6\text{H}_5\text{COONa}$  
(c) Chromium(III) nitrate, $\text{Cr(NO}_3\text{)}_3$

PLAN: We identify the cation and anion from the formula for each salt. Depending on an ion’s ability to react with water, the solution will be neutral (strong-acid anion with strong-base cation), acidic (weak-base cation with strong-acid anion), or basic (weak-acid anion and strong-base cation).

SOLUTION:

(a) $\text{K}^+$ is the cation of a strong base (KOH) while $\text{ClO}_4^-$ is the anion of a strong acid (HClO$_4$). This solution will be neutral.
(b) Na\(^+\) is the cation of a strong base (NaOH) while the benzoate anion (C\(_6\)H\(_5\)COO\(^-\)) is the anion of a weak acid (benzoic acid). The benzoate ion will react with H\(_2\)O to produce OH\(^-\) ions:

\[
\text{C}_6\text{H}_5\text{COO}^-(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{C}_6\text{H}_5\text{COOH}(aq) + \text{OH}^- (aq)
\]

This solution will be basic.

(c) NO\(_3^-\) is the anion of a strong acid (HNO\(_3\)) and will not react with H\(_2\)O to any great extent. Cr\(^{3+}\) is a small metal cation with a fairly high charge density. It will become hydrated and the hydrated ion will react with H\(_2\)O to form H\(_3\)O\(^+\) ions:

\[
\text{Cr(H}_2\text{O})_6^{3+}(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{Cr(H}_2\text{O})_5\text{OH}^{2+}(aq) + \text{H}_3\text{O}^+(aq)
\]

This solution will be acidic.
Salts of Weak Conjugate Acids and Weak Conjugate Bases

If a salt that consists of the **anion** of a **weak acid** and the **cation** of a **weak base**, the pH of the solution will depend on the relative acid strength or base strength of the ions.

\[
\text{NH}_4\text{CN} \\
\text{NH}_4^+(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \\
\text{CN}^-(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{HCN}(\text{aq}) + \text{OH}^-(\text{aq})
\]

- \(\text{NH}_4^+\) is the cation of a weak base, \(\text{NH}_3\).
- \(\text{CN}^-\) is the anion of a weak acid, \(\text{HCN}\).
The reaction that proceeds farther to the right determines the pH of the solution, so we need to compare the $K_a$ of NH$_4^+$ with the $K_b$ of CN$^-$. 

$$K_a \text{ of NH}_4^+ = \frac{K_w}{K_b \text{ of NH}_3} = \frac{1.0 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.7 \times 10^{-10}$$

$$K_b \text{ of CN}^- = \frac{K_w}{K_a \text{ of HCN}} = \frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5}$$

Since $K_b$ of CN$^-$ > $K_a$ of NH$_4^+$, CN$^-$ is a stronger base than NH$_4^+$ is an acid. A solution of NH$_4$CN will be basic.
All strong acids and bases are equally strong in water.

All strong acids dissociate completely to form $\text{H}_3\text{O}^+$, while all strong bases dissociate completely to form $\text{OH}^-$.

In water, the strongest acid possible is $\text{H}_3\text{O}^+$ and the strongest base possible is $\text{OH}^-$.

$\text{H}_2\text{O}$ exerts a leveling effect on any strong acid or base.
A Lewis base is any species that donates an electron pair to form a bond.

A Lewis acid is any species that accepts an electron pair to form a bond.

The Lewis definition views an acid-base reaction as the donation and acceptance of an electron pair to form a covalent bond.