According to the Brønsted–Lowry theory, all acid–base reactions can be written as equilibria involving the acid and base and their conjugates. All proton transfer reactions proceed from the stronger acid and base to the weaker acid and base.

**Predicting the Direction of Acid–Base Reactions**

- According to the Brønsted–Lowry theory, all acid–base reactions can be written as equilibria involving the acid and base and their conjugates.  

\[
\text{Conjugate base of the acid} + \text{Conjugate acid of the base} \rightleftharpoons \text{Stronger acid} + \text{Stronger base} \\
\text{Weaker acid} + \text{Weaker base}
\]

- All proton transfer reactions proceed from the stronger acid and base to the weaker acid and base.
When a weak acid is in solution, the products are a stronger conjugate acid and base. Therefore, equilibrium lies to the left.

All proton transfer reactions proceed from the stronger acid and base to the weaker acid and base.

In following equilibrium, will reactants or products be favored?

\[
\text{H}_3\text{PO}_4(\text{aq}) + \text{CH}_3\text{CO}_2(\text{aq}) \rightleftharpoons \text{H}_2\text{PO}_3(\text{aq}) + \text{CH}_3\text{CO}_2\text{H(}\text{aq})
\]
Predicting Direction of Acid–Base Reactions

In following equilibrium, will reactants or products be favored?

\[ K_a = 7.5 \times 10^{-5} \quad K_a = 1.8 \times 10^{-5} \]

\[ K_b = 5.6 \times 10^{-10} \quad K_b = 1.3 \times 10^{-12} \]

\[ \text{H}_3\text{PO}_4(\text{aq}) + \text{CH}_3\text{CO}_2(\text{aq}) \rightleftharpoons \text{H}_2\text{PO}_3(\text{aq}) + \text{CH}_3\text{CO}_2\text{H}(\text{aq}) \]

\[ K_a = 7.5 \times 10^{-5} \quad K_a = 1.8 \times 10^{-5} \]

Types: Acids–Base Reactions

Strong acid (HCl) + Strong base (NaOH)

\[ \text{HCl (aq)} + \text{NaOH (aq)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{NaCl (aq)} \]

Net ionic equation

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

Mixing equal molar quantities of a strong acid and strong base produces a neutral solution.
**Types: Acids–Base Reactions**

**Weak acid (HCN) + Strong base (NaOH)**

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

Mixing equal amounts (moles) of a strong base and a weak acid produces a salt whose anion is the conjugate base of the weak acid. The solution is basic, with the pH depending on \(K_b\) for the anion.

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

**Strong acid (HCl) + Weak base (NH\(_3\))**

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

Mixing equal amounts (moles) of a weak base and a strong acid produces a conjugate acid of the weak base. The solution is basic, with the pH depending on \(K_a\) for the acid.

\[
\text{NH}_4^+(aq) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{NH}_3(aq)
\]
**Types: Acids–Base Reactions**

Weak acid \((\text{CH}_3\text{CO}_2\text{H})\) + Weak base \((\text{NH}_3)\)

\[
\text{CH}_3\text{CO}_2\text{H}(\text{aq}) + \text{NH}_3(\text{aq}) \rightleftharpoons \text{CH}_3\text{CO}_2^-(\text{aq}) + \text{NH}_4^+(\text{aq})
\]

Mixing equal amounts (moles) of a weak acid and a weak base produces a salt whose cation is the conjugate acid of the weak base and whose anion is the conjugate base of the weak acid. The solution pH depends on the relative \(K_a\) and \(K_b\) values.

**Types: Acids–Base Reactions**

Weak acid + Weak base

- Product cation = conjugate acid of weak base.
- Product anion = conjugate base of weak acid.
- pH of solution depends on relative strengths of cation and anion.
Calculations with Equilibrium Constants

Determining $K$ from Initial Concentrations and pH

\[ \text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{NO}_2^-(\text{aq}) \]

\[ 0.10 \text{ M HNO}_2(\text{aq}) \quad \text{pH} = 2.17 \]

<table>
<thead>
<tr>
<th></th>
<th>[HNO$_3$]</th>
<th>[H$_3$O$^+$]</th>
<th>[NO$_2^-$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>0.10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Change</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Equilibrium</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Calculations with Equilibrium Constants

Determining $K$ from Initial Concentrations and pH

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

\[ 1.00 \text{ M H}_2\text{S}(\text{aq}) \quad K_a = 1.0 \times 10^{-7} \]

<table>
<thead>
<tr>
<th></th>
<th>[H$_2$S]</th>
<th>[H$_3$O$^+$]</th>
<th>[HS$^\text{-}$]</th>
</tr>
</thead>
</table>
Determining $K$ from Initial Concentrations and $\text{pH}$

In general, the approximation that

$$[\text{HA}]_{\text{equilibrium}} = [\text{HA}]_{\text{initial}} - x \approx [\text{HA}]_{\text{initial}}$$

is valid whenever $[\text{HA}]_{\text{initial}}$ is greater than or equal to $100 \times K_a$.

If this is not the case, the quadratic equation must be used.

Determining $pH$ after an acid/base reaction:

Calculate the hydronium ion concentration and $pH$ of the solution that results when 22.0 mL of 0.15 M acetic acid, $\text{CH}_3\text{CO}_2\text{H}$, is mixed with 22.0 mL of 0.15 M NaOH.
Calculations with Equilibrium Constants

Determining \( \text{pH} \) after an acid/base reaction:

Calculate the hydronium ion concentration and \( \text{pH} \) of the solution that results when 22.0 mL of 0.15 M acetic acid, \( \text{CH}_3\text{CO}_2\text{H} \), is mixed with 22.0 mL of 0.15 M NaOH.

**Solution:** From the volume and concentration of each solution, the moles of acid and base can be calculated. Knowing the moles after the reaction and the equilibrium constants, the concentration of \( \text{H}_3\text{O}^+ \) and \( \text{pH} \) can be calculated.

---

Polyprotic Acids & Bases

Because polyprotic acids are capable of donating more than one proton they present us with additional challenges when predicting the \( \text{pH} \) of their solutions.

For many inorganic polyprotic acids, the ionization constant for each successive loss of a proton is roughly \( 10^5 \) times smaller than the previous step. This implies that the \( \text{pH} \) of many inorganic polyprotic acids depends primarily on the hydronium ion generated in the first ionization step. The hydronium ion produced in the second step can be neglected.
Polyprotic Acids & Bases

Sulfurous acid, $\text{H}_2\text{SO}_3$, is a weak acid capable of providing two $\text{H}^+$ ions ($\text{pK}_{a1} = 1.9$, $\text{pK}_{a2} = 7.0$).

(a) What is the pH of a 0.45 M solution of $\text{H}_2\text{SO}_3$?
(b) What is the equilibrium concentration of the sulfite ion, $\text{SO}_3^{2-}$, in the 0.45 M solution of $\text{H}_2\text{SO}_3$?

Polyprotic Acids, cont.

As we have seen, several common acids can potentially donate more than one proton. Sulfuric ($\text{H}_2\text{SO}_4$) and phosphoric ($\text{H}_3\text{PO}_4$) acids are particularly prominent examples:

- $\text{H}_2\text{SO}_4$: $\text{pK}_{a1} < 0$; $\text{pK}_{a2} = 1.92$
- $\text{H}_3\text{PO}_4$: $\text{pK}_{a1} = 2.12$; $\text{pK}_{a2} = 7.21$; $\text{pK}_{a3} = 12.68$

What are the concentrations of all species in a 0.1 M phosphoric acid solution?
Features of Polyprotic Acids

H₃PO₄ is a representative example:

\[ pK_{a1} = 2.12; \ pK_{a2} = 7.21; \ pK_{a3} = 12.68 \]

At what pH are the concentrations of H₃PO₄ and H₂PO₄⁻ equal?

At that pH, what are the concentrations of HPO₄²⁻ and PO₄³⁻?

Tough question to answer directly: What is the pH of a H₂PO₄⁻ or HPO₄²⁻ salt solution? (e.g., K₂HPO₄ or KH₂PO₄ solution)

Easier: what’s the pH when [H₂PO₄⁻] = [PO₄³⁻]?

\[ K_{a2} = \frac{[H_3O^+][HPO_4^{2-}]}{[H_2PO_4^-]} \]

when [H₂PO₄⁻] = [PO₄³⁻],

\[ \frac{[H_3O^+][HPO_4^{2-}]}{K_{a2}} = K_{a3} \frac{[HPO_4^{2-}]}{[H_3O^+]} \Rightarrow \text{pH} = \frac{1}{2}(pK_{a2} + pK_{a3}) \]

But at this pH, [HPO₄²⁻] >> [H₂PO₄⁻] = [PO₄³⁻]
The concept of acid–base behavior advanced by Brønsted and Lowry in the 1920’s works well for reactions involving proton transfer. However, a more general acid–base concept, was developed by Gilbert N. Lewis in the 1930’s.

- A **Lewis acid** is a substance that can accept a pair of electrons from another atom to form a new bond.
- A **Lewis base** is a substance that can donate a pair of electrons to another atom to form a new bond.

\[
pH = \frac{1}{2}(pK_{a1} + pK_{a2})
\]

\[
pH = \frac{1}{2}(pK_{a2} + pK_{a3})
\]

\[
[H_3PO_4] = [H_2PO_4^-]
\]

\[
[H_2PO_4^-] = [H_2PO_4^{2-}]
\]

\[
[H_2PO_4^{2-}] = [PO_4^{3-}]
\]
The Lewis Concept of Acids & Bases

\[ A + B: \rightleftharpoons B: \rightarrow A \]

Acid Base Adduct

The product is often called an acid–base adduct. In Section 8.3, this type of chemical bond was called a coordinate covalent bond.

Lewis acid-base reactions are very common. In general, they involve Lewis acids that are cations or neutral molecules with an available, empty valence orbital and bases that are anions or neutral molecules with a lone electron pair.

---

The Lewis Concept of Acids & Bases

**Lewis acid**

a substance that accepts an electron pair

\[
\text{BF}_3, \text{the boron atom is surrounded by only three electron pairs}.
\]

**Lewis base**

a substance that donates an electron pair

\[
\text{H}_2\text{O, the N atom has three bond pairs and one lone pair of electrons}.
\]
**Reaction of a Lewis Acid & Lewis Base**

- New bond formed using electron pair from the Lewis base.
- Coordinate covalent bond
- Notice geometry change on reaction.

**The Lewis Concept of Acids & Bases**

The formation of a hydronium ion is an example of a Lewis acid / base reaction

\[
\ce{H^+ + \overset{\cdot}{O}H} \rightleftharpoons \ce{H\overset{\cdot}{O}H}
\]

ACID \hspace{2cm} BASE

The \( \text{H}^+ \) is an electron pair acceptor. Water with it’s lone pairs is a Lewis acid donor.
Lewis Acids & Bases

Metal cations often act as Lewis acids because of open d-orbitals.

\[
\text{Co}^{2+} \quad :\ddot{O} \quad H \quad \text{ACID}
\]

\[
\text{H} \quad \text{BASE}
\]

\[
\text{Co}^{2+} \quad :\ddot{O} \quad H
\]

\[
\text{H}
\]

\[
[H_3O]^+ \quad \text{aq}
\]

\[
\text{Be}^{2+} \quad \text{aq} \quad + \quad 4 \text{H}_2\text{O} \quad \rightarrow \quad \text{Be}_4\text{(H}_2\text{O})_4^{2+} \quad \text{aq}
\]
**Lewis Acids & Bases**

The combination of metal ions (Lewis acids) with Lewis bases such as H₂O and NH₃ leads to *Coordinate Complex ions.*

![Image of Cu²⁺(aq) + 4 NH₃(aq) → [Cu(NH₃)₄]²⁺(aq)
light blue → deep blue
Copper-ammonia coordinate covalent bond]

**Lewis Acids & Bases**

Aqueous solutions of Fe³⁺, Al³⁺, Cu²⁺, Pb²⁺, etc. are acidic through hydrolysis.

![Image of Al³⁺(aq) + H₂O(l) → [Al(H₂O)₅(OH)]²⁺(aq) + H₃O⁺(aq)]

This interaction weakens this bond

Another H₂O pulls this H away as H⁺
**Hydrolysis of Metal Complexes can give acidic solutions**

<table>
<thead>
<tr>
<th>Complex</th>
<th>pKₐ (n+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(H₂O)₆]³⁺</td>
<td>2.46</td>
</tr>
<tr>
<td>[Cr(H₂O)₆]³⁺</td>
<td>3.89</td>
</tr>
<tr>
<td>[Al(H₂O)₆]³⁺</td>
<td>4.85</td>
</tr>
<tr>
<td>[Fe(H₂O)₆]²⁺</td>
<td>5.89</td>
</tr>
<tr>
<td>[Cu(H₂O)₆]³⁺</td>
<td>7.49</td>
</tr>
<tr>
<td>[Ni(H₂O)₆]²⁺</td>
<td>9.03</td>
</tr>
</tbody>
</table>