We will cover the following topics:

1. Definition of Acids and Bases
2. Bronsted-Lowry Acids and Bases
Arrhenius Definition of Acids and Bases

An acid is a substance that reacts with water to produce hydronium ions, H\(_3\)O\(^+\).

A base is a substance that produces hydroxide ions, OH\(^-\), in water.

When an acid and base react, an ionic compound is produced as one of the products. We call ionic compounds “salts”.

Arrhenius Theory of Acid and Bases

Support for the Arrhenius concept comes from measurements of \(\Delta H^o\) of neutralization of any strong acid and base. Consider the following reactions:

\[
\text{NaOH(aq)} + \text{HCl(aq)} \rightarrow \text{NaCl(aq)} + \text{H}_2\text{O}(\ell) \quad \Delta H^o = -56 \text{ kJ/mol}
\]

\[
\text{LiOH(aq)} + \text{HBr(aq)} \rightarrow \text{LiBr(aq)} + \text{H}_2\text{O}(\ell) \quad \Delta H^o = -56 \text{ kJ/mol}
\]

If we write the net ionic equation for both of these reactions we see that they are the same

\[
\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(\ell)
\]
Monoprotic and Polyprotic acids

1. Monoprotic acids – capable of ionizing 1 H⁺ ion per molecule of acid.

Example:

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

\[
\text{CH}_3\text{COOH (aq) + H}_2\text{O (l) } \Rightarrow \text{H}_3\text{O}^+ \text{ (aq) + CH}_3\text{COO}^- \text{ (aq)}
\]

Strong acid = 100% dissociation into ions

Weak acid = partial dissociation into ions

2. Polyprotic acids – capable of ionizing more than one H⁺ ion per molecule of acid.

Example of a Diprotic acid:

\[
\text{H}_2\text{SO}_4 \text{ (aq) + H}_2\text{O (l) } \rightarrow \text{H}_3\text{O}^+ \text{ (aq) + HSO}_4^- \text{ (aq)}
\]

\[
\text{HSO}_4^- \text{ (aq) + H}_2\text{O (l) } \rightarrow \text{H}_3\text{O}^+ \text{ (aq) + SO}_4^{2-} \text{ (aq)}
\]

Example of a Triprotic acid:

\[
\text{H}_3\text{PO}_4 \text{ (aq) + H}_2\text{O (l) } \rightarrow \text{H}_3\text{O}^+ \text{ (aq) + H}_2\text{PO}_4^- \text{ (aq)}
\]

\[
\text{H}_2\text{PO}_4^- \text{ (aq) + H}_2\text{O (l) } \rightarrow \text{H}_3\text{O}^+ \text{ (aq) + HPO}_4^{2-} \text{ (aq)}
\]

\[
\text{HPO}_4^{2-} \text{ (aq) + H}_2\text{O (l) } \rightarrow \text{H}_3\text{O}^+ \text{ (aq) + PO}_4^{3-} \text{ (aq)}
\]

You should be able to write acid dissociation reactions. Pay attention to the charges on all the ions, and balance the reactions.
Monoprotic and Polyprotic bases

1. Monoprotic bases – capable of ionizing 1 OH⁻ ion per molecule of base.

Example:

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

Nitrogen compounds are bases because they dissolve in water to produce OH⁻ ions.

\[ \text{NH}_3 (aq) + \text{H}_2\text{O} (\ell) \rightarrow \text{NH}_4^+ (aq) + \text{OH}^- (aq) \]
\[ \text{CH}_3\text{NH}_2 (aq) + \text{H}_2\text{O} (\ell) \rightarrow \text{CH}_3\text{NH}_3^+ (aq) + \text{OH}^- (aq) \]

You should be able to write base dissociation reactions.

Pay attention to the charges on all the ions, and balance the reactions.

Weak base = partial dissociation into ions

Strong base = 100% dissociation into ions

2. Polyprotic bases – capable of ionizing more than one OH⁻ ion per molecule of base.

Example:

\[ \text{Ca(OH)}_2 (aq) \rightarrow \text{Ca}^{2+} (aq) + 2 \text{OH}^- (aq) \]
\[ \text{Al(OH)}_3 (aq) \rightarrow \text{Al}^{3+} (aq) + 3 \text{OH}^- (aq) \]
### Acids, Bases and Salts

#### Hebden – Unit 4 (page 109-182)

In general,

1. Ionization of an acid in water

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

2. Ionization of a base in water

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

   or

   \[ \text{B(OH)}_x (aq) \rightarrow \text{B}^{x+} (aq) + x \text{OH}^- (aq) \]

### Brønsted-Lowry Acids and Bases

When neutralization reaction occurs in aqueous solution, Arrhenius’ definition of acid and base works well.

\[ \text{HCl (aq)} + \text{NH}_3 (aq) \rightarrow \text{NH}_4\text{Cl (aq)} + \text{H}_2\text{O(l)} \]

**Hydrochloric acid** (base) **ammonium chloride**

**An acid as a substance that reacts with water to produce \(\text{H}_3\text{O}^+\).**

**A base that reacts with water to produce \(\text{OH}^-\).**
Brønsted-Lowry Acids and Bases

This same neutralization reaction can occur when it is not in an aqueous medium. Therefore, Arrhenius’s definition of an acid and a base is too restrictive.

Example: Neutralization reaction of reactants in gas phase

\[
\text{HCl (g) + NH}_3\text{ (g) } \rightarrow \text{NH}_4\text{Cl (s)}
\]

Hydrogen ammonia smoke containing chloride gas tiny crystals of ammonium chloride

We need a broader definition!

What is in common between the gaseous and aqueous reactions?

1. Both involve a transfer of a H\(^+\) from one reactant to another.

In solution, HCl is completely ionized and the H\(^+\) ion is transferred from HCl to NH\(_3\).

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

In gas phase,

\[
\text{NH}_3\text{(g) + HCl (g) } \rightarrow \text{NH}_4^+\text{Cl}^-\text{(s)}
\]
Brønsted-Lowry Acids and Bases

- View acid-base reactions as simply the transfer of H⁺ (protons) from one species to another.

Brønsted-Lowry Acids and Bases Definitions

Acid is a proton donor.
Base is a proton acceptor.

\[ \text{HCl (g)} + \text{NH}_3 (g) \rightarrow \text{NH}_4^+ \text{ Cl}^- (s) \]

This species donates a proton to NH₃, therefore, it is an acid.
This species accepts a proton, therefore, it is a base.

In general,

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

**CONJUGATE ACID-BASE PAIRS**

Two species that differ by H⁺ are called a *conjugate pair*.

There is a whole table of Brønsted-Lowry Acids and Bases.
Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Brønsted-Lowry Acids and Bases

<table>
<thead>
<tr>
<th>Name of Acid</th>
<th>Acid</th>
<th>Base</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>perchloric</td>
<td>$\text{HClO}_4$</td>
<td>$\text{H}^+ + \text{ClO}_4^-$</td>
<td>very large</td>
</tr>
<tr>
<td>hydrochloric</td>
<td>$\text{HCl}$</td>
<td>$\text{H}^+ + \text{Cl}^-$</td>
<td>very large</td>
</tr>
<tr>
<td>hydrobromic</td>
<td>$\text{HBr}$</td>
<td>$\text{H}^+ + \text{Br}^-$</td>
<td>very large</td>
</tr>
<tr>
<td>hydroiodic</td>
<td>$\text{HI}$</td>
<td>$\text{H}^+ + \text{I}^-$</td>
<td>very large</td>
</tr>
<tr>
<td>nitric</td>
<td>$\text{HNO}_3$</td>
<td>$\text{H}^+ + \text{NO}_3^-$</td>
<td>very large</td>
</tr>
<tr>
<td>sulphuric</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$\text{H}^+ + \text{HSO}_4^-$</td>
<td>very large</td>
</tr>
<tr>
<td>hydronium ion</td>
<td>$\text{H}_2\text{O}^+$</td>
<td>$\text{H}^+ + \text{H}_2\text{O}^-$</td>
<td>1.0</td>
</tr>
<tr>
<td>iodic</td>
<td>$\text{HIO}$</td>
<td>$\text{H}^+ + \text{IO}^-$</td>
<td>$1.7 \times 10^{-3}$</td>
</tr>
<tr>
<td>oxalic</td>
<td>$\text{H}_2\text{C}_2\text{O}_4$</td>
<td>$\text{H}^+ + \text{HC}_2\text{O}_4^-$</td>
<td>$5.9 \times 10^{-2}$</td>
</tr>
<tr>
<td>sulphurous ($\text{SO}_4 + \text{H}_2\text{O}$)</td>
<td>$\text{H}_2\text{SO}_4$</td>
<td>$\text{H}^+ + \text{HSO}_4^-$</td>
<td>$1.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>hydrogen sulphate ion</td>
<td>$\text{H}_2\text{SO}_4^-$</td>
<td>$\text{H}^+ + \text{SO}_4^{2-}$</td>
<td>$1.2 \times 10^{-2}$</td>
</tr>
<tr>
<td>phosphoric</td>
<td>$\text{H}_3\text{PO}_4$</td>
<td>$\text{H}^+ + \text{H}_2\text{PO}_4^-$</td>
<td>$7.5 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Brønsted-Lowry Conjugate Acids-Bases Pairs

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{H}_2\text{O}$</td>
<td>$\text{OH}^-$</td>
</tr>
<tr>
<td>$\text{NH}_4^+$</td>
<td>$\text{NH}_3$</td>
</tr>
<tr>
<td>$\text{HCO}_3^-$</td>
<td>$\text{CO}_3^{2-}$</td>
</tr>
<tr>
<td>$\text{H}_3\text{O}^+$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{N}_2\text{H}_4$</td>
<td>$\text{N}_2\text{H}_3^-$</td>
</tr>
<tr>
<td>$\text{H}_3\text{O}^+$</td>
<td>$\text{H}_2\text{O}$</td>
</tr>
<tr>
<td>$\text{NH}_3$</td>
<td>$\text{NH}_2^-$</td>
</tr>
<tr>
<td>$\text{H}_2\text{CO}_3$</td>
<td>$\text{HCO}_3^-$</td>
</tr>
<tr>
<td>$\text{HPO}_4^{2-}$</td>
<td>$\text{PO}_4^{3-}$</td>
</tr>
</tbody>
</table>
Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

We will cover the following topics:

1. Amphiprotic Substance
2. Amphoteric Compounds

1. Amphiprotic Substance
A substance that can act either as a proton acceptor or a proton donor.

All amphiprotic substances contain a hydrogen atom.

Example 1 – Water, H₂O

\[
\begin{align*}
H_2O (l) + HCl (aq) & \rightarrow H_3O^+ (aq) + Cl^- (aq) \\
\text{base} & \quad \text{acid} \\
H_2O (l) + NH_3 (aq) & \rightarrow NH_4^+ (aq) + OH^- (aq) \\
\text{acid} & \quad \text{base}
\end{align*}
\]
1. Amphiprotic Substance

A substance that can act either as a proton acceptor or a proton donor.

All amphiprotic substances contain a hydrogen atom.

Example 2 – Bicarbonate, $\text{HCO}_3^-$

\[
\text{HCO}_3^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq}) \rightarrow \text{H}_2\text{CO}_3 (\text{aq}) + \text{H}_2\text{O} (\ell)
\]

base          acid

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

acid          base

You should be able to write these equations.

Example 3 – hydrogen sulfate ion, $\text{HSO}_4^-$

\[
\text{HSO}_4^- (\text{aq}) + \text{H}_3\text{O}^+ (\text{aq}) \rightarrow \text{H}_2\text{SO}_4 (\text{aq}) + \text{H}_2\text{O} (\ell)
\]

base          acid

\[
\text{HSO}_4^- (\text{aq}) + \text{OH}^- (\text{aq}) \rightarrow \text{SO}_4^{2-} (\text{aq}) + \text{H}_2\text{O} (\ell)
\]

acid          base

You should be able to write these equations.
2. Amphoteric Substance

• A compound that can react as either an acid or a base.
• “Ampho-” is Greek, it means “both”.
• Metals have amphoteric oxides. (eg – ZnO, Al(OH)₃)

Example 1 – Zinc oxide, ZnO

Reacts with acid: ZnO(aq) + 2H₃O⁺(aq) → Zn²⁺(aq) + 3H₂O(l)
acts as a base

Reacts with base:
ZnO (aq) + 2 OH⁻ (aq) + H₂O (l) → [Zn(OH)₄]²⁻ (aq)
acts as an acid zincate ion

Example 2 – Water, H₂O

Reacts with acid: H₂O (l) + HCl (aq) → H₃O⁺ (aq) + Cl⁻ (aq)
acts as a base

Reacts with base: H₂O (l) + NH₃ (aq) → NH₄⁺ (aq) + OH⁻ (aq)
acts as an acid
2. Amphoteric Substance

• A compound that can react as either an acid or a base.
• “Ampho-” is Greek, it means “both”.
• Metals have amphoteric oxides. (eg – ZnO, Al(OH)₃)

Example 3 – Aluminum hydroxide, Al(OH)₃

Reacts with acid:

\[
\text{Al(OH)}_3 \text{ (aq)} + 3\text{HCl (aq)} \rightarrow \text{AlCl}_3 \text{ (aq)} + 3\text{H}_2\text{O (ℓ)}
\]

acts as a base

Reacts with base:

\[
\text{Al(OH)}_3 \text{ (aq)} + \text{OH}^- \text{ (aq)} \rightarrow [\text{Al(OH)}_4]^- \text{ (aq)}
\]

acts as an acid aluminate ion

\[
\text{acts as a base}
\]

Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Strong acids

An acid which dissociates 100% into its ions in a water solution. 

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

The [H⁺] (or [H₃O⁺]) concentration of a 0.10 M HCl solution is 0.10 M.

For monoprotic strong acids [acid] = [H⁺]

A common notation to express [H⁺] is pH, where

\[
pH = -\log [H^+] = -\log 0.10 = 1.00
\]
Recall the pH scale

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

For an increase in 1 pH unit, the solution's \([H^+]\) decreases 10x.

**Acids, Bases and Salts**

Hebden – Unit 4 (page 109-182)

**Strong acids**

<table>
<thead>
<tr>
<th>Acid</th>
<th>(K_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perchloric</td>
<td>very large</td>
</tr>
<tr>
<td>Hydrofluoric</td>
<td>very large</td>
</tr>
<tr>
<td>Hydrobromic</td>
<td>very large</td>
</tr>
<tr>
<td>Hydrochloric</td>
<td>very large</td>
</tr>
<tr>
<td>Nitric</td>
<td>very large</td>
</tr>
<tr>
<td>Sulphuric</td>
<td>very large</td>
</tr>
</tbody>
</table>

These are strong acids.

Dissociation is a single arrow to produce ions.
Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

Weak acids
An acid which dissociates less than 100% into its ions in a water solution.

CH₃COOH (aq) + H₂O (l) ⇌ H₃O⁺ (aq) + CH₃COO⁻ (aq)

The [H⁺] (or [H₃O⁺]) concentration of a 0.10 M CH₃COOH solution is LESS THAN 0.10 M.

Therefore,

pH > 1.00

In weak acids [acid] ≠ [H⁺]

Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

Weak acids
An acid which dissociates less than 100% into its ions in a water solution.

HA (aq) + H₂O (l) ⇌ H₃O⁺ (aq) + A⁻ (aq)

K_a = \frac{[H₃O⁺][A⁻]}{[HA]}
Weak acids

<table>
<thead>
<tr>
<th></th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_3)O(^+)</td>
<td>1.0</td>
</tr>
<tr>
<td>HIO(_3)</td>
<td>1.7 \times 10^{-4}</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>very small</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>very small</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>very small</td>
</tr>
</tbody>
</table>

These are weak acids except the bottom two.

These last two are too weak to act as acids in water.

Note the single arrows pointing backward because the forward dissociation never occurs.
(a) A strong acid HA is completely ionized in water.
(b) A weak acid HB exists mostly as undissociated HB molecules in water.

Note that the water molecules are not shown in this figure.

Strong bases
A base which dissociates 100% into its ions in a water solution.

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

The [OH\(^-\)] concentration of a 0.10 M NaOH solution is 0.10 M.

For NaOH, \([\text{base}] = [\text{OH}^-]\)

A common notation to express [OH\(^-\)] is pOH, where

\[ \text{pOH} = -\log [\text{OH}^-] = -\log 0.10 = 1.00 \]
Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

**pH and pOH scales**

<table>
<thead>
<tr>
<th>pH</th>
<th>pOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td>10</td>
<td>4</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
</tr>
<tr>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>13</td>
<td>1</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
</tr>
</tbody>
</table>

**NEUTRAL**

- [H⁺] > [OH⁻]  
- [H⁺] = [OH⁻]  
- [OH⁻] > [H⁺]

Convert between pH and pOH:  
\[ \text{pH} + \text{pOH} = 14 \text{ at } 25°C \]

Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

**Strong bases**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Reaction</th>
<th>Dissociation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>( \text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^- )</td>
<td>very small</td>
</tr>
<tr>
<td>Hydroxide ion</td>
<td>( \text{OH}^- \rightarrow \text{H}^+ + \text{O}^{2-} )</td>
<td>very small</td>
</tr>
<tr>
<td>Ammonia</td>
<td>( \text{NH}_3 \rightarrow \text{H}^+ + \text{NH}_4^- )</td>
<td>very small</td>
</tr>
</tbody>
</table>

These are strong bases.

Any substance which dissociates completely to produce \( \text{OH}^- \), \( \text{O}^{2-} \), or \( \text{NH}_2^- \) is a strong base.

Examples:
- Group 1 hydroxides: LiOH, NaOH, KOH, RbOH, CsOH
- Group 2 hydroxides: Mg(OH)$_2$, Ba(OH)$_2$, Sr(OH)$_2$
Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

Strong bases

• For NaOH, \([\text{OH}^-] = [\text{base}]\)
• For Ba(OH)\(_2\), \([\text{OH}^-] = 2 \times [\text{base}]\)

Salts which produce \(\text{O}^{2-}\) are strong bases.

Example: \(\text{CaO (s)} \rightarrow \text{Ca}^{+2} (\text{aq}) + \text{O}^{2-} (\text{aq})\)

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

Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

Weak bases

A base which dissociates less than 100% into its ions in a water solution.

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

The [OH\(^-\)] concentration of a 0.10 M NH\(_3\) solution is LESS THAN 0.10 M.

Therefore,

\(\text{pOH} > 1.00\)

In weak bases \([\text{base}] \neq [\text{OH}^-]\)
Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Weak bases
A base which dissociates less than 100% into its ions in a water solution.

\[ B (aq) + H_2O (l) \rightleftharpoons BH^+ (aq) + OH^- (aq) \]

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

Conjugate bases of strong acids are VERY weak bases.

These are weak bases, found on the right side of the table.
Amphiprotic Species

- Found on both sides of the table (e.g., HSO₄⁻)
- Can act as acids or as bases
- When found on the left, it is an acid.

\[ K_a \]

HCO₃⁻ is a weaker acid than phenol and a stronger acid than hydrogen peroxide.

\[ \text{Acid Strength increases} \]

Amphiprotic Species

- Found on both sides of the table (e.g., HSO₄⁻)
- Can act as acids or as bases
- When found on the right, it is a base.

\[ K_a \]

HCO₃⁻ is a weaker base than citrate ion and a stronger base than Al(H₂O)₆(OH)²⁺.
We will work with the reference table

**RELATIVE STRENGTHS OF BRØNSTED-LOWRY ACIDS AND BASES**

to determine the Acid-Base Equilibria and Relative Strengths of Acids and Bases.

By examining the relative strengths of the acids on both sides of the equilibrium, we can determine which side of the equilibrium is favoured.
1. When H$_2$CO$_3$ and SO$_3^{2-}$ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

\[
\text{H}_2\text{CO}_3 (aq) + \text{SO}_3^{2-} (aq) \rightleftharpoons \text{HCO}_3^- (aq) + \text{HSO}_3^- (aq)
\]

This can only donate a H$^+$ ion. It is an **ACID**.

This ion can only act as a **BASE**, accept a H$^+$ ion.

As a result...

\[\text{HCO}_3^-\text{ is the conjugate base of H}_2\text{CO}_3.\]

\[\text{HSO}_3^-\text{ is the conjugate acid of SO}_3.\]

Compare the $K_a$ of the two acids

\[
\begin{align*}
\text{H}_2\text{CO}_3 & \quad \Leftrightarrow \quad \text{H}^+ + \text{HCO}_3^- \quad \ldots \ldots \ldots \ldots \quad 4.3 \times 10^{-7} \\
\text{HSO}_3^- & \quad \Leftrightarrow \quad \text{H}^+ + \text{SO}_3^{2-} \quad \ldots \ldots \ldots \ldots \quad 1.0 \times 10^{-7}
\end{align*}
\]

H$_2$CO$_3$ is a slightly stronger acid than HSO$_3^-$. The equilibrium will favour the products.
1. When $H_2CO_3$ and $SO_3^{2-}$ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

$$H_2CO_3 (aq) + SO_3^{2-} (aq) \rightleftharpoons HCO_3^- (aq) + HSO_3^- (aq)$$

acid base conjugate base conjugate acid

What is the value of $K$ for this equilibrium?

$$K = \frac{K_a (HCO_3^-)}{K_a (HSO_3^-)} = \frac{4.3 \times 10^{-7}}{1.0 \times 10^{-7}} = 4.3 > 1$$

Since $K > 1$, equilibrium favors products.

2. When $H_2PO_4^-$ and $CO_3^{2-}$ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

$$H_2PO_4^- (aq) + CO_3^{2-} (aq) \rightleftharpoons HCO_3^- (aq) + HPO_4^{2-} (aq)$$

This is an amphiprotic ion. It can donate or accept a $H^+$ ion.

This ion can only act as a BASE, accept a $H^+$ ion.

After considering, in this mixture, $H_2PO_4^-$ will act as an acid.

As a result ...

$HCO_3^-$ is the conjugate acid of $CO_3^{2-}$.

$HPO_4^{2-}$ is the conjugate base of $H_2PO_4^-$. 

$HCO_3^-$ is the conjugate acid of $CO_3^{2-}$.
2. When $\text{H}_2\text{PO}_4^-$ and $\text{CO}_3^{2-}$ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

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

Acid Base Conjugate Acid Conjugate Base

Compare the $K_a$ of the two acids

$$\text{H}_2\text{PO}_4^- \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \quad 6.2 \times 10^{-8}$$

$$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad 5.6 \times 10^{-11}$$

$\text{H}_2\text{PO}_4^-$ is a stronger acid than $\text{HCO}_3^-$. The equilibrium will favour the products.

3. When $\text{HSO}_4^-$ and $\text{NH}_3$ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

$$\text{HSO}_4^-(aq) + \text{NH}_3(aq) \rightleftharpoons \text{NH}_4^+(aq) + \text{SO}_4^{2-}(aq)$$

This is an amphiprotic ion. It can donate or accept a $\text{H}^+$ ion.

This can only act as a BASE, accept a $\text{H}^+$ ion.

After considering, in this mixture, $\text{HSO}_4^-$ will act as an acid.

$\text{NH}_4^+$ is the conjugate acid of $\text{NH}_3$.

$\text{SO}_4^{2-}$ is the conjugate base of $\text{HSO}_4^-$. As a result...
3. When \( \text{HSO}_4^- \) and \( \text{NH}_3 \) are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

\[
\text{HSO}_4^- (aq) + \text{NH}_3 (aq) \rightleftharpoons \text{NH}_4^+ (aq) + \text{SO}_4^{2-} (aq)
\]

<table>
<thead>
<tr>
<th>acid</th>
<th>base</th>
<th>conjugate acid</th>
<th>conjugate base</th>
</tr>
</thead>
</table>

Compare the \( K_a \) of the two acids

\[
\begin{align*}
\text{HSO}_4^- & \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} & 1.2 \times 10^{-2} \\
\text{NH}_4^+ & \rightleftharpoons \text{H}^+ + \text{NH}_3 & 5.6 \times 10^{-10}
\end{align*}
\]

\( \text{HSO}_4^- \) is a stronger acid than \( \text{NH}_4^+ \). The equilibrium will favour the products.

4. When \( \text{HSO}_4^- \) and \( \text{H}_2\text{PO}_4^- \) are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

Both \( \text{HSO}_4^- \) and \( \text{H}_2\text{PO}_4^- \) are amphiprotic ions. Which will play the role of an acid? Let’s compare their \( K_a \) values.

\[
\begin{align*}
\text{HSO}_4^- & \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} & 1.2 \times 10^{-2} \\
\text{H}_2\text{PO}_4^- & \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} & 6.2 \times 10^{-8}
\end{align*}
\]

\( \text{HSO}_4^- \) is a stronger acid than \( \text{H}_2\text{PO}_4^- \).

\( \text{HSO}_4^- \) will act as an acid donating protons to \( \text{H}_2\text{PO}_4^- \).

---

After considering, in this mixture, \( \text{HSO}_4^- \) will act as an acid. \( \text{H}_2\text{PO}_4^{2-} \) will act as the base.
4. When $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

$$\text{HSO}_4^-(aq) + \text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}_3\text{PO}_4(aq) + \text{SO}_4^{2-}(aq)$$

$K_a$ of $\text{HSO}_4^-$ is bigger. It has the higher tendency to donate $\text{H}^+$. Comparatively, it has less tendency to donate $\text{H}^+$. As a result...

$\text{HSO}_4^-$ is the conjugate base of $\text{H}_2\text{PO}_4^-$. $\text{SO}_4^{2-}$ is the conjugate base of $\text{HSO}_4^-$. After considering, in this mixture, $\text{HSO}_4^-$ will act as an acid.

**Acids, Bases and Salts**

Hebden – Unit 4 (page 109-182)

4. When $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

$$\text{HSO}_4^-(aq) + \text{H}_2\text{PO}_4^-(aq) \rightleftharpoons \text{H}_3\text{PO}_4(aq) + \text{SO}_4^{2-}(aq)$$

Acid $\xrightarrow{\text{base}}$ $\text{HSO}_4^-$ $\xrightarrow{\text{conjugate acid}}$ $\text{H}_3\text{PO}_4$ $\xrightarrow{\text{conjugate base}}$ $\text{SO}_4^{2-}$

Compare the $K_a$ of the two acids

$$\begin{align*}
\text{HSO}_4^- & \rightleftharpoons \text{H}^+ + \text{SO}_4^{2-} \quad 1.2 \times 10^{-2} \\
\text{H}_3\text{PO}_4 & \rightleftharpoons \text{H}^+ + \text{H}_2\text{PO}_4^- \quad 7.5 \times 10^{-3}
\end{align*}$$

$\text{HSO}_4^-$ is a stronger acid than $\text{H}_3\text{PO}_4^-$. The equilibrium will favour the products.
5. When CH₃COOH and NH₃ are mixed, an equilibrium is set up. Which side of the equilibrium is favoured?

\[
\text{CH}_3\text{COOH} (aq) + \text{NH}_3 (aq) \rightleftharpoons \text{CH}_3\text{COO}^- (aq) + \text{NH}_4^+ (aq)
\]

Acid base conjugate base conjugate acid

Compare the \( K_a \) of the two acids

- \[
\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^- \quad 1.8 \times 10^{-5}
\]
- \[
\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3 \quad 5.6 \times 10^{-10}
\]

CH₃COOH is a stronger acid than NH₄⁺. The equilibrium will favour the products.

6. Consider an amino acid, an equilibrium is set up between the amine group, R-NH₂, and the carboxylic acid group, R-COOH. Which side of the equilibrium is favoured?

\[
\text{H}_2\text{NCHRCOOH} (aq) \rightleftharpoons \text{H}_2\text{NCHRCOO}^- (aq)
\]

Base acid conjugate acid conjugate base

Compare the \( K_a \) of the two acids

- \[
\text{CH}_3\text{COOH} \rightleftharpoons \text{H}^+ + \text{CH}_3\text{COO}^- \quad 1.8 \times 10^{-5}
\]
- \[
\text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3 \quad 5.6 \times 10^{-10}
\]

CH₃COOH is a stronger acid than NH₄⁺. The equilibrium will favour the products (i.e. a double charged species).
**Direction of Reaction Example**

Predict the direction favored in each of the following acid-base reactions. That is, does the reaction tend to go more in the forward or in the reverse direction?

- a) \( \text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{NH}_3 \) \hspace{1cm} \text{Forward}
- b) \( \text{HSO}_4^- + \text{NO}_3^- \rightleftharpoons \text{HNO}_3 + \text{SO}_4^{2-} \) \hspace{1cm} \text{Reverse}
- c) \( \text{HSO}_3^- + \text{CH}_3\text{COO}^- \rightleftharpoons \text{SO}_3^{2-} + \text{CH}_3\text{COOH} \) \hspace{1cm} \text{Reverse}
- d) \( \text{CH}_3\text{COOH} + \text{Cr(H}_2\text{O})_6\text{(OH)}^{2+} \rightleftharpoons \text{Cr(H}_2\text{O})_6^{3+} + \text{CH}_3\text{COO}^- \) \hspace{1cm} \text{Reverse}
- e) \( \text{HNO}_2 + \text{ClO}_4^- \rightleftharpoons \text{HClO}_4 + \text{NO}_2^- \) \hspace{1cm} \text{Reverse}
- f) \( \text{H}_2\text{CO}_3 + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{HCO}_3^- \) \hspace{1cm} \text{Forward}

*In aqueous solutions, \( \text{H}_3\text{O}^+ \) (aq) & \( \text{OH}^- \) (aq) are the strongest acids and bases that exist.*

Stronger bases react with water to form \( \text{OH}^- \) (aq)
\[
\text{O}^2^- \text{(aq)} + \text{H}_2\text{O} (\ell) \rightarrow \text{OH}^- \text{(aq)} + \text{OH}^- \text{(aq)}
\]

Stronger acids react with water to form \( \text{H}_3\text{O}^+ \) (aq).
\[
\text{HCl} \text{(aq)} + \text{H}_2\text{O} (\ell) \rightarrow \text{H}_3\text{O}^+ \text{(aq)} + \text{Cl}^- \text{(aq)}
\]

This is known as the **Leveling Effect**
The Self-Ionization of Water

\[
\begin{align*}
H_2O(l) + H_2O(l) & \rightleftharpoons H_3O^+(aq) + OH^-(aq) \\
K &= \frac{[H_3O^+][OH^-]}{[H_2O][H_2O]} \\
K_w &= K[H_2O][H_2O] = [H_3O^+][OH^-] = 1 \times 10^{-14} \text{ at } 25^\circ C
\end{align*}
\]

Consider:

HA(aq) + H_2O(l) ⇌ A^-(aq) + H_3O^+(aq) \quad K_a

A^-(aq) + H_2O(l) ⇌ HA(aq) + OH^-(aq) \quad K_b

\[
K_a K_b = \left( \frac{[A^-][H_3O^+]}{[HA]} \right) \left( \frac{[HA][OH^-]}{[A^-]} \right) = [H_3O^+][OH^-] = K_w
\]

\[
K_w = K_a K_b
\]
pH and pOH

- The potential of the hydrogen ion was defined in 1909 as the negative of the logarithm of $[H^+]$.

$$\text{pH} = -\log[H_3O^+] \quad \text{pOH} = -\log[OH^-]$$

$$K_W = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25°C$$

$$-\log K_W = -\log[H_3O^+]-\log[OH^-]= -\log(1.0 \times 10^{-14})$$

$$pK_W = \text{pH} + \text{pOH} = -(-14)$$

$$pK_W = \text{pH} + \text{pOH} = 14 \text{ at } 25°C$$

Concentration and pH and pOH Examples at 25°C

<table>
<thead>
<tr>
<th></th>
<th>$[H^+]$</th>
<th>$[OH^-]$</th>
<th>pH</th>
<th>pOH</th>
<th>Acidic/Basic</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 5.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15 M HNO₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.0100 M Ca(OH)₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0x10⁻¹⁰ M Ca(OH)₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Concentration and pH and pOH Examples at 25°C

<table>
<thead>
<tr>
<th>pH</th>
<th>[H⁺]</th>
<th>[OH⁻]</th>
<th>pH</th>
<th>pOH</th>
<th>Acidic/Basic</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.52</td>
<td>3.0x10⁻⁶ M</td>
<td>3.3x10⁻⁹ M</td>
<td>5.52</td>
<td>8.48</td>
<td>Acidic</td>
</tr>
<tr>
<td>0.15 M HNO₃</td>
<td>0.15 M</td>
<td>6.7x10⁻¹⁴ M</td>
<td>0.82</td>
<td>13.18</td>
<td>Acidic</td>
</tr>
<tr>
<td>0.0100 M Ca(OH)₂</td>
<td>5.00x10⁻¹³ M</td>
<td>2.00x10⁻² M</td>
<td>12.301</td>
<td>1.699</td>
<td>Basic</td>
</tr>
<tr>
<td>1.0x10⁻¹⁰ M Ca(OH)₂</td>
<td>1x10⁻⁷ M</td>
<td>1x10⁻⁷ M</td>
<td>7</td>
<td>7</td>
<td>Neutral</td>
</tr>
</tbody>
</table>

Strong Acid and Bases Examples

1. Calculate the pH of a solution of 0.400 g of HI in 500. ml of solution.

2. Calculate the the mass of Sr(OH)₂ which must be dissolved in 600. ml of solution to make a pH of 12.00.
Weak Acid and Bases Examples

1. Butyric acid, $\text{HC}_4\text{H}_7\text{O}_2$ (or $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$) is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of $\text{HC}_4\text{H}_7\text{O}_2$ is found to have a pH of 2.72. Determine $K_a$ for butyric acid.

2. Calculate the pH of a 0.20 M solution of KF, $K_b$ for F$^-$ is $1.5 \times 10^{-11}$.

Hydrolysis

is the reaction between water and the ions contained in the water solution. When this occurs, this could result in producing an acidic or basic solution.

Spectator ions do NOT undergo hydrolysis. They are:

1. Group 1 (alkali metals): Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Fr$^+$
2. Group 2 (alkaline-earth metals): Be$^{2+}$, Mg$^{2+}$, Ca$^{2+}$, Ba$^{2+}$, Sr$^{2+}$
3. Conjugate bases of strong acids: ClO$_4^-$, I$^-$, Br$^-$, Cl$^-$, NO$_3^-$
**Acids, Bases and Salts**  
Hebden – Unit 4 (page 109-182)

Cation that undergo hydrolysis

- **NH₄⁺**, ammonia

\[
\text{NH}_4^+ \rightleftharpoons H^+ + \text{NH}_3 \quad \text{K} = 5.6 \times 10^{-10}
\]

Hydrolysis equation:

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

Hydrated cations that undergo hydrolysis

- Transition metals have smaller ions and bigger charges
- This attracts H₂O molecules
- Example – Fe³⁺ or iron (III) ions forms

\[
\text{Fe}^{3+} (aq) + 6 \text{H}_2\text{O} (\ell) \rightarrow \text{Fe(H}_2\text{O)}_6^{3+} (aq)
\]

*Hexaquoiron, or iron (III) ion is a weak acid.*

- Other hydrated ions are chromium (III) and aluminum (III) ions

\[
\begin{align*}
\text{Cr(H}_2\text{O)}_6^{3+} & \rightleftharpoons \text{H}^+ + \text{Cr(H}_2\text{O)}_5(\text{OH})^{2+} \quad \text{K} = 1.5 \times 10^{-4} \\
\text{Al(H}_2\text{O)}_6^{3+} & \rightleftharpoons \text{H}^+ + \text{Al(H}_2\text{O)}_5(\text{OH})^{2+} \quad \text{K} = 1.4 \times 10^{-5}
\end{align*}
\]
Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Anions that undergo hydrolysis

\[
\begin{align*}
\text{IO}_3^- (aq) + H_2O (l) & \rightleftharpoons \text{HIO}_3 (aq) + OH^- (aq) \\
\text{NO}_2^- (aq) + H_2O (l) & \rightleftharpoons \text{HNO}_2 (aq) + OH^- (aq) \\
\text{CH}_3\text{COO}^- (aq) + H_2O (l) & \rightleftharpoons \text{CH}_3\text{COOH} (aq) + OH^- (aq)
\end{align*}
\]

All ions in this section can undergo hydrolysis.

Anions that are not amphiprotic will act as weak bases in water.

Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Anions that undergo hydrolysis

Examples of net ionic hydrolysis equations are:

\[
\begin{align*}
\text{IO}_3^- (aq) + H_2O (l) & \rightleftharpoons \text{HIO}_3 (aq) + OH^- (aq) \\
\text{NO}_2^- (aq) + H_2O (l) & \rightleftharpoons \text{HNO}_2 (aq) + OH^- (aq) \\
\text{CH}_3\text{COO}^- (aq) + H_2O (l) & \rightleftharpoons \text{CH}_3\text{COOH} (aq) + OH^- (aq)
\end{align*}
\]
Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Anions that undergo hydrolysis

\[ \text{\(H_2O\)} \rightleftharpoons \text{\(H^+ + OH^-\)} \quad 1.0 \times 10^{-14} \]
\[ \text{\(CH^-\)} \leftarrow \text{\(H^+ + OH^-\)} \quad \text{very small} \]
\[ \text{\(NH_3\)} \leftarrow \text{\(H^+ + NH_2^-\)} \quad \text{very small} \]

These 2 ions act as STRONG Bases. They undergo 100% hydrolysis to form OH\(^{-}\) ions.

Anions that are not amphiprotic will act as weak bases in water.

Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Anions that do not undergo hydrolysis

- \(\text{HClO}_4 \rightarrow \text{H}^+ + \text{ClO}_4^-\) very large
- \(\text{HI} \rightarrow \text{H}^+ + \text{I}^-\) very large
- \(\text{HBr} \rightarrow \text{H}^+ + \text{Br}^-\) very large
- \(\text{HCl} \rightarrow \text{H}^+ + \text{Cl}^-\) very large
- \(\text{HNO}_3 \rightarrow \text{H}^+ + \text{NO}_3^-\) very large

These 5 ions do NOT undergo hydrolysis. They are spectators.
Amphiprotic anions that undergo hydrolysis

These anions start with “H” and have a “-” charge.

Examples: HSO₄⁻, HSO₃⁻, H₂PO₄⁻, HPO₄²⁻, HS⁻ etc.

Amphiprotic anions hydrolyze as **acids** to produce H₃O⁺, but they also hydrolyze as **bases** to produce OH⁻. Compare the $K_a$ and $K_b$ values to determine the predominant hydrolysis.

Find the $K_a$ of the ion by looking for the ion on the LEFT side of the acid table.

Find the $K_b$ of the ion by looking for the ion on the RIGHT side of the acid table. ($K_b = K_w/K_a$ (conjugate acid))

---

1. Is the salt NaCl acidic, basic or neutral in water?

NaCl (s) → Na⁺ (aq) + Cl⁻ (aq)

Na⁺ and Cl⁻ ions are spectator ions.

As a result ...

No hydrolysis reaction occurs. Solution is neutral.
2. Is the salt NaF acidic, basic or neutral in water? What is the net ionic equation?

\[ \text{NaF (s)} \rightarrow \text{Na}^+ (aq) + \text{F}^- (aq) \]

$\text{Na}^+ \text{ ions are spectator ions.}$

$\text{F}^- \text{ ions are found on the right side of the acid table.}$

It is a weak base.

\[ \text{HF} \rightleftharpoons \text{H}^+ + \text{F}^- \quad 3.5 \times 10^{-4} \]

As a result ...

$\text{F}^- \text{ undergoes hydrolysis reaction.}$

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

Solution is basic.

---

3. Is the salt NH$_4$NO$_3$ acidic, basic or neutral in water? What is the net ionic equation?

\[ \text{NH}_4\text{NO}_3 (s) \rightarrow \text{NH}_4^+ (aq) + \text{NO}_3^- (aq) \]

$\text{NO}_3^- \text{ ions are spectator ions.}$

$\text{NH}_4^+ \text{ ions are found on the left side of the acid table.}$

It is a weak acid.

\[ \text{NH}_4^+ \rightleftharpoons \text{H}^+ + \text{NH}_3 \quad 5.6 \times 10^{-10} \]

As a result ...

$\text{NH}_4^+ \text{ undergoes hydrolysis reaction.}$

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

Solution is acidic.
4. Is the salt NaHC₂O₄ acidic, basic or neutral in water? What is the net ionic equation?

\[
\text{NaHC}_2\text{O}_4 (s) \rightarrow \text{Na}^+ (aq) + \text{HC}_2\text{O}_4^- (aq)
\]

- **Na⁺ ions are spectator ions.**
- **HC₂O₄⁻ ions are found on the right and left side of the acid table.**
- It can either be a weak acid or a weak base.

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4 & \rightleftharpoons \text{H}^+ + \text{HC}_2\text{O}_4^- \quad 5.9 \times 10^{-2} \\
\text{HC}_2\text{O}_4^- & \rightleftharpoons \text{H}^+ + \text{C}_2\text{O}_4^{2-} \quad 6.4 \times 10^{-5}
\end{align*}
\]

As a result, compare \( K_a \) and \( K_b \) values of HC₂O₄⁻.

\[ K_a = 6.4 \times 10^5; \quad K_b = \frac{10^{-14}}{5.9 \times 10^{-2}} = 1.7 \times 10^{13} \]

\( K_a > K_b \).

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

Solution is acidic.

5. Is the salt NH₄NO₂ acidic, basic or neutral in water? Write the net ionic equation.

\[
\text{NH}_4\text{NO}_2 (s) \rightarrow \text{NH}_4^+ (aq) + \text{NO}_2^- (aq)
\]

- **NH₄⁺ ions are found on the left side of the acid table.**
- **NO₂⁻ ions are found on the right side of the acid table.**

\[
\begin{align*}
\text{NH}_4^+ & \rightleftharpoons \text{H}^+ + \text{NH}_3 \quad 5.6 \times 10^{-10} \\
\text{HNO}_2 & \rightleftharpoons \text{H}^+ + \text{NO}_2^- \quad 4.6 \times 10^{-4}
\end{align*}
\]

As a result, compare \( K_a \) of NH₄⁺ \( K_b \) of NO₂⁻.

\[ K_a = 5.6 \times 10^{10}; \quad K_b = \frac{10^{-14}}{4.6 \times 10^{-4}} = 2.2 \times 10^{11} \]

\( K_a > K_b \). Solution is acidic.
6. Is the HCO$_3^-$ ion acidic, basic or neutral in water?

HCO$_3^-$ ions are found on the right and left side of the acid table.

\[
\begin{align*}
H_2CO_3 & \rightleftharpoons H^+ + HCO_3^- & 4.3 \times 10^{-7} \\
HCO_3^- & \rightleftharpoons H^+ + CO_3^{2-} & 5.6 \times 10^{-11}
\end{align*}
\]

As a result, compare $K_a$ and $K_b$ of HCO$_3^-$. 

\[
K_a = 5.6 \times 10^{10}, \quad K_b = \frac{10^{-14}}{4.3 \times 10^7} = 2.3 \times 10^8
\]

$K_b > K_a$. 

\[
\text{HCO}_3^- (aq) + H_2O (\ell) \rightleftharpoons H_2CO_3 (aq) + OH^- (aq)
\]

Solution is basic.

Salt Examples

Predict whether the following solutions are acidic or basic?

a) NaOCl  
Na$^+$ no hydrolysis, OCl$^-$ is conjugate base of HOCl.  
Therefore solution is basic.

b) KCl  
K$^+$ no hydrolysis, Cl$^-$ no hydrolysis.  
Therefore solution is neutral.

c) NH$_4$Br  
Br$^-$ no hydrolysis (HBr is strong acid),  
NH$_4^+$ is a weak acid. Therefore solution is acidic.

d) NH$_4$CN  
Both NH$_4^+$ and CN$^-$ hydrolyze in aqueous solutions. 
Must compare the values of $K_a$(NH$_4^+$) = 5.6x10$^{-10}$  
and $K_b$(CN$^-$) = 2.0x10$^{-5}$. Since $K_b$\(>\)\(K_a\) the solution is basic.
Is the salt Na₂CO₃ acidic, basic or neutral in water?

Write the net ionic equation.

\[
\text{Na}_2\text{CO}_3 (s) \rightarrow 2 \text{Na}^+ (aq) + \text{CO}_3^{2-} (aq)
\]

\text{Na}^+ \text{ ions are spectator ions.}
\text{CO}_3^{2-} \text{ ions are found on the right side of the acid table.}
\text{It is a weak base.}

\[
\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-} \quad \text{K} = 5.6 \times 10^{-11}
\]

As a result ...

\text{CO}_3^{2-} \text{ undergoes hydrolysis reaction. The net ionic equation is}
\text{CO}_3^{2-} (aq) + \text{H}_2\text{O} (\ell) \rightleftharpoons \text{HCO}_3^- (aq) + \text{OH}^- (aq)
\text{Solution is basic.}
Calculate the pH of 0.30 M Na₂CO₃.

Step 1: Identify the ions involved.

Na₂CO₃ (s) → 2 Na⁺ (aq) + CO₃²⁻ (aq)

Step 2: Write the net ionic equation for the hydrolysis. Set up ICE table.

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

<table>
<thead>
<tr>
<th></th>
<th>CO₃²⁻(aq)</th>
<th>H₂O (ℓ)</th>
<th>⇌ HCO₃⁻(aq)</th>
<th>OH⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[I]</td>
<td>0.30</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>[C]</td>
<td>- x</td>
<td>+ x</td>
<td>+ x</td>
<td></td>
</tr>
<tr>
<td>[E]</td>
<td>0.30 - x</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Stoichiometric ratio
Calculate the pH of 0.30 M Na$_2$CO$_3$.

**Step 3: Determine the $K_b$ for the base hydrolysis.**

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

Look up in the acid table the $K_a$ for HCO$_3^-$

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

\[
K_b = \frac{K_w}{K_a(\text{HCO}_3^-)} = \frac{1.0 \times 10^{-14}}{5.6 \times 10^{-11}} = 1.786 \times 10^{-4}
\]

**Step 4: Write the $K_b$ expression for the base hydrolysis.**

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

\[
K_b = \frac{[\text{HCO}_3^-] \cdot [\text{OH}^-]}{[\text{CO}_3^{2-}]}\]
Calculate the pH of 0.30 M Na₂CO₃.

**Step 5:** Substitute in the equilibrium concentrations from the ICE table.

<table>
<thead>
<tr>
<th></th>
<th>CO₃²⁻(aq) + H₂O(ℓ) ⇌ HCO₃⁻(aq) + OH⁻(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[I]</td>
<td>0.30</td>
</tr>
<tr>
<td>[C]</td>
<td>-x</td>
</tr>
<tr>
<td>[E]</td>
<td>0.30 - x</td>
</tr>
</tbody>
</table>

\[
K_b = \frac{[HCO_3^-] \cdot [OH^-]}{[CO_3^{2-}]} = \frac{x^2}{0.30 - x} = 1.786 \times 10^{-4}
\]

Step 6: Solve for x, where \( x = [OH^-] \).

\[
\frac{x^2}{0.30} = 1.786 \times 10^{-4}
\]

Use assumption \( 0.30 - x \approx 0.30 \) because \( [0.30] > 1000 \times 1.786 \times 10^{-4} \)

\[
[OH^-] = x = 7.319 \times 10^{-3} \text{ M}
\]
Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Calculate the pH of 0.30 M Na₂CO₃.

Step 7: From the [OH⁻], calculate the pOH.

\[ \text{pOH} = -\log (7.319 \times 10^{-3}) = 2.1355 \]

Step 8: Convert pOH to pH.

\[ \text{pH} = 14 - \text{pOH} = 14 - 2.1355 = 11.86 \]

Step 9: Check that your answer makes sense.
We expect CO₃²⁻ ions will undergo base hydrolysis. pH > 7.

Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

Dissolve 45.0 g of NH₄Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH₄Cl is 53.5 g/mole.
Dissolve 45.0 g of NH\(_4\)Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH\(_4\)Cl is 53.5 g/mole.

**Step 1: Determine the concentration of the solution.**

\[
\frac{45.0 \text{ g}}{53.5 \text{ g/mole}} = 0.841 \text{ mole} \\
\frac{0.841 \text{ mole}}{1.50 \text{ L}} = 0.561 \text{ M NH}_4\text{Cl}
\]

**Step 2: Identify the ions involved.**

\[
\text{NH}_4\text{Cl (s) \rightarrow NH}_4^+ (aq) + \text{Cl}^- (aq)
\]

*Found on the left side of the acid table; undergo acid hydrolysis*  
*Spectator ion*
Dissolve 45.0 g of NH₄Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH₄Cl is 53.5 g/mole.

Step 3: Write the net ionic equation for the hydrolysis.

Set up ICE table.

\[
\text{NH}_4^+ (aq) + H_2O (\ell) \rightleftharpoons \text{NH}_3 (aq) + H_3O^+ (aq)
\]

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>C</th>
<th>E</th>
</tr>
</thead>
<tbody>
<tr>
<td>[I]</td>
<td>0.561</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>[C]</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>[E]</td>
<td>0.561 -x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

Step 4: Determine the \( K_b \) for the base hydrolysis.

\[
\text{NH}_4^+ (aq) + H_2O (\ell) \rightleftharpoons \text{NH}_3 (aq) + H_3O^+ (aq)
\]

Look up in the acid table the \( K_a \) for NH₄⁺

\[
\text{NH}_4^+ \rightleftharpoons H^+ + \text{NH}_3 \quad 5.6 \times 10^{-10}
\]
Dissolve 45.0 g of NH₄Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH₄Cl is 53.5 g/mole.

**Step 5: Write the $K_a$ expression for the acid hydrolysis.**

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

$$K_a = \frac{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

**Step 6: Substitute in the equilibrium concentrations from the ICE table.**

<table>
<thead>
<tr>
<th></th>
<th>NH₄⁺ (aq) + H₂O (l) ⇌ NH₃ (aq) + H₃O⁺ (aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[I]</td>
<td>0.561</td>
</tr>
<tr>
<td>[C]</td>
<td>- x</td>
</tr>
<tr>
<td>[E]</td>
<td>0.561 - x</td>
</tr>
</tbody>
</table>

\[
\begin{align*}
&\text{[I]} \quad 0.561 \\
&\text{[C]} \quad - x \\
&\text{[E]} \quad 0.561 - x
\end{align*}
\]

\[
K_a = \frac{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.561 - x} = 5.6 \times 10^{-10}
\]
Dissolve 45.0 g of NH₄Cl in 1.50 L of water. What is the pH of this solution? Molar mass of NH₄Cl is 53.5 g/mole.

Step 7: Solve for x, where x = [H₃O⁺].

\[ K_a = \frac{[\text{NH}_3] \cdot [\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = \frac{x^2}{0.561 - x} = 5.6 \times 10^{-10} \]

Make assumption: 0.561 – x ≈ 0.561

\[ K_a = \frac{x^2}{0.561} = 5.6 \times 10^{-10} \]

\[ [\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-5} \text{ M} \]

Check assumption: [Initial] > 1000 x \( K_a \)

Assumption is valid because 0.561 > 1000 x 5.6 x 10⁻¹⁰

Step 8: Convert to pH.

\[ [\text{H}_3\text{O}^+] = x = 1.8 \times 10^{-5} \text{ M} \]

\[ \text{pH} = - \log (1.8 \times 10^{-5}) = 4.74 \]
Titrations

- **Equivalence point:**
  - The point in the reaction at which both acid and base have been consumed.
  - Neither acid nor base is present in excess.
- **End point:**
  - The point at which the indicator changes color.
- **Titrant:**
  - The solution added to the solution in the flask.
- **Titration Curve:**
  - A plot of pH of the solution being analyzed as a function of the amount of titrant added.

Acid-Base Indicators

- Color of some substances depends on the pH.
  - $\text{HIn(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{In}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
  - $>90\%$ acid form the color appears to be the acid color
  - $>90\%$ base form the color appears to be the base color
  - Intermediate color is seen in between these two states.
- Complete color change occurs over 2 pH units
- Marks the **end point** of a titration by changing color.
- The **equivalence point** is not necessarily the same as the **end point**.
The acid and base forms of the indicator phenolphthalein. In the acid form (HIn), the molecule is colorless. When a proton (plus H₂O) is removed to give the base form (In⁻), the color changes to pink.
Titration of a Strong Acid with a Strong Base

- The pH has a low value at the beginning.
- The pH changes slowly
  - until just before the equivalence point.
- The pH rises sharply
  - perhaps 6 units per 0.1 mL addition of titrant.
- The pH rises slowly again.
- Any Acid-Base Indicator will do.
  - As long as color change occurs between pH 4 and 10.

The pH curve for the titration of 100.0 mL of 0.10 M HCl with 0.10 M NaOH.

Note:
- At the equivalence point pH = 7
- Either indicator will give a fairly accurate result.
For the titration of a strong base with a strong acid the titration curve is just flipped over.

The pH curve for the titration of 100.0 mL of 0.50 M NaOH with 1.0 M HCl.

**Weak Acid - Strong Base Titration**

- **Step 1** - A stoichiometry problem - reaction is assumed to run to completion - then determine remaining species.

- **Step 2** - An equilibrium problem - determine position of weak acid equilibrium and calculate pH.
Weak Acid - Strong Base Titration

The pH curve for the titration of 50.0 mL of 0.100 M \( \text{HC}_2\text{H}_3\text{O}_2 \) with 0.100 M NaOH.

Note:
- At the equivalence point pH > 7
- Choice of indicator is important
- \( pK_a = \text{pH at the point halfway to the equivalence point} \)
- The pH is fairly constant around halfway to the equivalence point i.e it is a buffer solution

Comparison of strong and weak acid titration curves.
Acids, Bases and Salts
Hebden – Unit 4 (page 109-182)

The pH curves for the titrations of 50.0-mL samples of 0.10 M acids with various $K_a$ values with 0.10 M NaOH.

For the titration of a weak base with a strong acid the titration curve is just flipped over.

The pH curve for the titration of 100.0 mL of 0.050 M NH₃ with 0.10 M HCl.

Note at equivalence point pH < 7
Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

Titration of a Weak Polyprotic Acid

\[ \text{NaOH} \]
\[ \text{H}_3\text{PO}_4 \rightarrow \text{H}_2\text{PO}_4^- \rightarrow \text{HPO}_4^{2-} \rightarrow \text{PO}_4^{3-} \]

Buffer Solutions

- Two component systems that change pH only slightly on addition of acid or base.
  - The two components must not neutralize each other but must neutralize strong acids and bases.

- A weak acid and it’s conjugate base.
- A weak base and it’s conjugate acid

- After addition of strong acid or base, deal with stoichiometry first, then equilibrium.
How A Buffer Works

The Henderson-Hasselbalch Equation

A variation of the ionization constant expression.

Consider a hypothetical weak acid, HA, and its salt NaA:

\[
HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)
\]

\[
K_a = \frac{[H^+][A^-]}{[HA]} \quad \Rightarrow \quad -\log(K_a) = -\log[H^+] - \log[A^-]
\]

\[
pK_a = \text{pH} - \log\left(\frac{[A^-]}{[HA]}\right) \quad \text{or} \quad \text{pH} = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)
\]

\[
\text{pH} = pK_a + \log\left(\frac{\text{conjugate base}}{\text{conjugate acid}}\right)
\]
Acids, Bases and Salts
Hebden – Unit 4  (page 109-182)

The Henderson-Hasselbalch Equation

- Only useful when you can use initial concentrations of acid and salt.
  - This limits the validity of the equation.

- Limits can be met by:

\[ 0.1 < \frac{[A^-]}{[HA]} < 10 \]

and both \([A^-] > 10K_a\) and \([HA] > 10K_a\)

---

Characteristics of the Henderson-Hasselbalch Equation

- pH depends only on the ratio \([A^-]/[HA]\)
  - This means that the pH of a buffer solution does not change on dilution.

- When \([A^-] = [HA]\) then \(pH = pK_a\). This is also the point where the ratio changes least upon the addition of either acid or base. Therefore a system is best at buffering at a \(pH = pK_a\).

- pH changes as the Log of the ratio \([A^-]/[HA]\). Therefore pH is not very sensitive to the value of \([A^-]/[HA]\).

- The larger the value of \([A^-]\) and \([HA]\) the more acid or base that can be added without significantly changing the pH (i.e. the greater the buffering capacity of the solution).
Buffer Solutions

Consider the case of acetic acid

\[
\text{CH}_3\text{COOH}(aq) + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ (aq) + \text{CH}_3\text{COO}^- (aq)
\]

\[ pK_a = 4.75 \]

<table>
<thead>
<tr>
<th>\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}</th>
<th>\text{pH}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>3.75</td>
</tr>
<tr>
<td>0.5</td>
<td>4.45</td>
</tr>
<tr>
<td>1</td>
<td>4.75</td>
</tr>
<tr>
<td>2</td>
<td>5.05</td>
</tr>
<tr>
<td>10</td>
<td>5.75</td>
</tr>
</tbody>
</table>

Preparing a Buffer Solution of a Desired pH

- What mass of NaC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} must be dissolved in 0.300 L of 0.25 M HC\textsubscript{2}H\textsubscript{3}O\textsubscript{2} \( K_a = 1.8 \times 10^{-5} \) to produce a solution with pH = 5.09? (Assume that the solution volume is constant at 0.300 L)