Chapter 15
ACID-BASE EQUILIBRIA
(Cont.)

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gastric juice (human stomach)</td>
<td>1.0–3.0</td>
</tr>
<tr>
<td>Limes</td>
<td>1.8–2.0</td>
</tr>
<tr>
<td>Lemons</td>
<td>2.2–2.4</td>
</tr>
<tr>
<td>Soft drinks</td>
<td>2.0–4.0</td>
</tr>
<tr>
<td>Plums</td>
<td>2.8–3.0</td>
</tr>
<tr>
<td>Wines</td>
<td>2.8–3.8</td>
</tr>
<tr>
<td>Apples</td>
<td>2.9–3.3</td>
</tr>
<tr>
<td>Peaches</td>
<td>3.4–3.6</td>
</tr>
<tr>
<td>Cherries</td>
<td>3.2–4.0</td>
</tr>
<tr>
<td>Beers</td>
<td>4.0–5.0</td>
</tr>
<tr>
<td>Rainwater (unpolluted)</td>
<td>5.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Substance</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human blood</td>
<td>7.3–7.4</td>
</tr>
<tr>
<td>Egg whites</td>
<td>7.6–8.0</td>
</tr>
<tr>
<td>Milk of magnesia</td>
<td>10.5</td>
</tr>
<tr>
<td>Household ammonia</td>
<td>10.5–11.5</td>
</tr>
<tr>
<td>4% NaOH solution</td>
<td>14</td>
</tr>
</tbody>
</table>

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**Summary:** pH calculations of strong acids and strong bases

1. At relatively high [S.A] or high [S.B.], i.e. ≥ 10^{-6} M, pH is calculated from [S.A.] or [S.B.]

2. In very dilute [S.A] or [S.B.], i.e. ≤ 10^{-8} M, dissociation of water is more important, so the pH is 7.

**Question:** How do we know if a given acid is strong or weak?

**Know the following by heart:** You have to be able to name them too.

There are only six (6) strong acids to remember: HCl, HBr, HI, H_2SO_4, HNO_3, HClO_4

- Perchloric acid

There are only six (6) strong bases to remember: LiOH, NaOH, KOH, Ca(OH)_2, Sr(OH)_2, Ba(OH)_2
Determining the pH of solutions

Solutions of weak acids (W.A.)
➢ Ionization is incomplete; Equilibrium is set up

Ionization (dissociation) equation:

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

Or simply:

\[
\text{HA}_{(aq)} \rightleftharpoons \text{H}^+_{(aq)} + \text{A}^-_{(aq)}
\]

where \( K_a \) is the acid ionization (or dissociation) constant

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

➢ The \( K_a \) for W.A. is < 1.

---

**TABLE 15.5 Acid Ionization Constants (\( K_a \)) for Some Monoprotic Weak Acids at 25°C**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Formula</th>
<th>Structural Formula</th>
<th>Ionization Reaction</th>
<th>( K_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorous acid</td>
<td>HClO₂</td>
<td>( \text{H} - \text{O} - \text{Cl} - \text{O} )</td>
<td>( \text{HClO}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}<em>3\text{O}^+</em>{(aq)} + \text{ClO}<em>2^-</em>{(aq)} )</td>
<td>( 1.1 \times 10^{-2} )</td>
</tr>
<tr>
<td>Nitrous acid</td>
<td>HNO₂</td>
<td>( \text{H} - \text{O} = \text{N} = \text{O} )</td>
<td>( \text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}<em>3\text{O}^+</em>{(aq)} + \text{NO}<em>2^-</em>{(aq)} )</td>
<td>( 4.6 \times 10^{-4} )</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>HF</td>
<td>( \text{H} - \text{F} )</td>
<td>( \text{HF}(\text{aq}) + \text{H}<em>2\text{O}(l) \rightleftharpoons \text{H}<em>3\text{O}^+</em>{(aq)} + \text{F}^-</em>{(aq)} )</td>
<td>( 3.5 \times 10^{-4} )</td>
</tr>
<tr>
<td>Formic acid</td>
<td>HCHO₂</td>
<td>( \text{H} - \text{O} - \text{C} = \text{H} )</td>
<td>( \text{HCHO}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}<em>3\text{O}^+</em>{(aq)} + \text{CHO}<em>2^-</em>{(aq)} )</td>
<td>( 1.8 \times 10^{-4} )</td>
</tr>
<tr>
<td>Benzoic acid</td>
<td>( \text{H}_2\text{C}_6\text{H}_5\text{O}_2 )</td>
<td>( \text{H} - \text{O} - \text{C} - \text{C} = \text{C} \text{CH} )</td>
<td>( \text{HC}_6\text{H}_5\text{O}_2(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}<em>3\text{O}^+</em>{(aq)} + \text{C}_6\text{H}_5\text{O}<em>2^-</em>{(aq)} )</td>
<td>( 6.5 \times 10^{-5} )</td>
</tr>
</tbody>
</table>
Example: What is the H$_3$O$^+$ concentration and pH of a 0.10 M solution of hypochlorous acid, HOCl, $K_a = 3.5 \times 10^{-8}$?

- Note that the $K_a$ is a small number (i.e. HOCl is a weak acid. Start with the equilibrium equation:

  \[
  \begin{align*}
  K_a & \quad \text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OCl}^- \\
  \text{or} & \quad \text{HOCl} \_\text{(aq)} \rightleftharpoons \text{H}^+ \_\text{(aq)} + \text{OCl}^- \_\text{(aq)}
  \end{align*}
  \]

- HOCl is W.A.; only a fraction of 0.10 M HOCl will dissociate, i.e. we can set up our ICE table as:

  \[
  \begin{array}{ccc}
  \text{HOCl} + \text{H}_2\text{O}_{(l)} & \rightleftharpoons & \text{H}_3\text{O}^+ + \text{OCl}^- \\
  \text{I:} & 0.10 & 0 & 0 \\
  \text{C:} & -x & +x & +x \\
  \text{E:} & (0.10 - x) & x & x
  \end{array}
  \]
The $K_a$ expression is:

$$K_a = \frac{[OCl^-][H_3O^+]}{[HOCl]} = \frac{(x)(x)}{(0.10 - x)}$$

$$3.5 \times 10^{-8} = \frac{x^2}{(0.10 - x)}$$

Assuming $x << 0.10$ (since $K_a$ is very small) and solving for $x$, we get:

$$x = 5.92 \times 10^{-5} \text{ M} = [H_3O^+] = [OCl^-]$$

*Check:* Since $5.9 \times 10^{-5} << 0.10$ our assumption is valid. We calculate pH as:

$$pH = -\log (5.9_2 \times 10^{-5}) = 4.23$$

**Weak Acid Equilibria – Cont.**

**Exercise:** Calculate the pH of a $1.50 \times 10^{-2}$ M formic acid, HCO$_2$H. ($pK_a = 3.745$).

**Answer:** $pH = 2.808$

**HINT:** You must first determine $K_a$ from $pK_a$. *How?*
Determining $K_a$ from Measured pH

*Example:* A student measured the pH of a 0.10 M solution of formic acid, HCOOH, to be 2.38 at 25 °C. Calculate $K_a$ for formic acid at 25 °C.

*Answer:* $K_a = 1.8 \times 10^{-4}$
Percent Ionization of a Weak Acid

The *percent ionization* of a weak acid HA refers to the percentage of HA in ionized form, $H^+$ (and $A^-$)

$$\text{% ionization} = \frac{[H_3O^+]_{eq}}{[HA]_{initial}} \times 100$$

*Example*: What is percent of HOCl in ionized form in the previous example? (Recall that $[H^+] = 5.92 \times 10^{-5}$ M and initial [HOCl] = 0.10 M)

*Answer*: 0.059 % ionized
Weak Base Equilibria: Hydrolysis

- Recall that B-L bases are $\text{H}^+$ acceptor.
- In aqueous solutions, a weak base “grabs” a $\text{H}^+$ from water, forming its conjugate acid and $\text{OH}^-$. This reaction is called **hydrolysis**.

For a monobasic species, $B$, the **hydrolysis equation** is:

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

The equilibrium constant expression for this reaction is:

The hydrolysis reaction of each of the following bases:

- Carbonate, $\text{CO}_3^{2-}$
- Bicarbonate, $\text{HCO}_3^-$
- Sulfate, $\text{SO}_4^{2-}$
- Phosphate, $\text{PO}_4^{3-}$

Note: Add a $+1$ charge to the base to determine the charge of the conjugate acid.
**Determining pH of Solutions of Weak Bases**

Ammonia is the most commonly used weak base. The hydrolysis of ammonia is written as:

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-
\]

**Weak base**

The \( K_b \) expression for \( \text{NH}_3 \) can be written as:

\[
K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}
\]

Exercise: Calculate the concentration of \( \text{OH}^- \) in a 0.15 M solution of \( \text{NH}_3 \). \( K_b \) for \( \text{NH}_3 \) is \( 1.8 \times 10^{-5} \) at 25 \(^\circ\)C. What is the pH of this solution?

\[
\begin{align*}
\text{I:} & \quad 0.15 & \quad 0 & \quad 0 \\
\text{C:} & \quad -y & \quad +y & \quad +y \\
\text{E:} & \quad (0.15 - y) & \quad y & \quad y
\end{align*}
\]

\( K_b \) and pH can be expressed as:

\[
K_b = \frac{y^2}{(M_B - y)} \quad \text{and} \quad \text{pH} = 14.00 - \text{pOH} = 14.00 - (-\log [\text{OH}^-])
\]

or

\[
\text{pH} = 14.00 - \log (y)
\]
Relationship Between $K_a$ and $K_b$

Recall: *Conjugate species* = related by one H (as H⁺)

- The **stronger the acid** the **weaker its conj. base**
- Similarly, the stronger the base the weaker its conj. acid

<table>
<thead>
<tr>
<th>Strongest acid</th>
<th>$K_a$</th>
<th>Weakest base</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄⁻ + H₂O $\rightarrow$ 1 $\rightarrow$ H₂O⁺ + ClO₄⁻</td>
<td>$\gg 1$</td>
<td>H₂O⁺ + Cl⁻</td>
<td></td>
</tr>
<tr>
<td>HCl + H₂O $\rightarrow$ 1 $\rightarrow$ H₂O⁺ + Cl⁻</td>
<td>$\gg 1$</td>
<td>H₃O⁺ + Cl⁻</td>
<td></td>
</tr>
<tr>
<td>H₃PO₄ + H₂O $\rightarrow$ 7.11 x 10⁻³ $\rightarrow$ H₂O⁺ + H₂PO₄⁻</td>
<td>$\gg 1$</td>
<td>H₃O⁺ + H₂PO₄⁻</td>
<td></td>
</tr>
<tr>
<td>HC₂H₃O₂ + H₂O $\rightarrow$ 1.75 x 10⁻⁵ $\rightarrow$ H₃O⁺ + C₂H₃O₂⁻</td>
<td>$\gg 1$</td>
<td>H₃O⁺ + C₂H₃O₂⁻</td>
<td></td>
</tr>
<tr>
<td>NH₄⁺ + H₂O $\rightarrow$ 5.70 x 10⁻¹⁰ $\rightarrow$ H₃O⁺ + NH₃</td>
<td>$\gg 1$</td>
<td>H₃O⁺ + NH₃</td>
<td></td>
</tr>
</tbody>
</table>

Relationship Between $K_a$ and $K_b$

- The $K_a$ of an acid is also related to the $K_b$ of its conj. base, i.e.

For **conjugate acid-base pairs**:

\[
K_a \times K_b = K_w \quad \text{p}K_a + \text{p}K_b = 14.00
\]

Exercises:
(1) Calculate the $K_b$ for CO₃²⁻ if $K_a$ for HCO₃⁻ is 5.6 x 10⁻¹¹.
(2) Hydrofluoric acid, HF, has a pKₐ of 3.17. Calculate $K_b$ for fluoride ion, F⁻.

**Answers:** (1) $K_b = 1.8 \times 10^{-4}$; (2) $K_b = 1.5 \times 10^{-11}$
Importance of pH Control

What if pH is not controlled?

- Hyperacidic stomach
- Highly acidic soil $\Rightarrow$ low crop yield
- Air pollutants $\Rightarrow$ acid rain
  - Acidic lakes/rivers $\Rightarrow$ fish kills; erosion of statues; vegetation dies

*There must be a way to control pH*
Acid rain: a significant problem in the Northeastern U.S.

Damage Caused by Acid Rain

Damage to aquatic life

In some sensitive lakes and streams, acidification has completely eradicated fish species, such as the brook trout, leaving these bodies of water barren. In fact, hundreds of the lakes in the Adirondacks surveyed in the NSWS have acidity levels indicative of chemical conditions unsuitable for the survival of sensitive fish species.
Damage to vegetation and outdoor artwork (limestone)

Ways of Controlling pH

1) Through **neutralization** reactions = acid-base reactions

Ex. \[ \text{HCl} + \text{antacid (a carbonate)} \rightarrow \text{salt} + \text{H}_2\text{O} \]

Always produced in neutralization

Writing Neutralization Reactions

1) The metal from the base is always written (or named) first.
2) The metal from the base replaces the hydrogen of the acid.

\[
\begin{align*}
\text{HCl} &\quad + \quad \text{NaOH} \quad \rightarrow \quad \text{NaCl} \quad + \quad \text{HOH} \quad \quad \text{(or } \text{H}_2\text{O)} \\
\text{HNO}_3 &\quad + \quad \text{KOH} \quad \rightarrow \quad \text{KNO}_3 \quad + \quad \text{H}_2\text{O} \\
\text{HCN} &\quad + \quad \text{NaOH} \quad \rightarrow \quad \text{NaCN} \quad + \quad \text{H}_2\text{O}
\end{align*}
\]

Ways of Controlling pH (Cont.)

2) Through the action of **buffers**

- Substances that resist drastic changes in pH. HOW?
- They consist of a mixture of a **weak acid** and its **conjugate base** (i.e. an acid-base pair).

Ex. The pH of blood is maintained by a biological buffer, a mixture of **carbonic acid** and **bicarbonate ions**.
Ways of Controlling pH: *Action of Buffers* (Cont.)

**Hypoventilation**
More CO\(_2\) in lungs, more carbonic acid in blood = acidosis

**Hyperventilation**
Less CO\(_2\) in lungs, less carbonic acid in blood = alkalosis

- During **alkalosis** (blood pH rises) the acid component \(H_2CO_3\) of our biological buffer neutralizes the excess base and restores the pH to around 7.4, the normal pH of blood.

- During **acidosis** (blood pH drops), the base component \(HCO_3^-\) neutralizes the excess acid and restores the pH to around 7.4.

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**Acid-Base Properties of Salts**
Recall: Acids and bases can be electrically neutral (ex. HCl, NH$_3$) or charged (ex. NH$_4^+$, CO$_3^{2-}$)

- Implication: **Salts**, ionic compounds formed from neutralization reactions, can be acidic, basic or neutral solutions.
  - The anion or the cation of a salt, or both, can react with water (= **hydrolysis** reaction)
  - The pH of salt solution depends on the strengths of the original acids and bases

---

**Salts – Cont.**

Q. What is the pH of an aqueous solution of a salt?

- The pH of the salt depends on the strengths of the original acids and bases

<table>
<thead>
<tr>
<th>Acid</th>
<th>Base</th>
<th>Salt pH</th>
<th>Example of salt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td>Strong</td>
<td>7 (Neutral)</td>
<td>NaCl, KNO$_3$, CaBr$_2$</td>
</tr>
<tr>
<td>Weak</td>
<td>Strong</td>
<td>&gt; 7 (Basic)</td>
<td>Na$_2$CO$_3$, K$_3$PO$_4$</td>
</tr>
<tr>
<td>Strong</td>
<td>Weak</td>
<td>&lt; 7 (Acidic)</td>
<td>NH$_4$Cl, CH$_3$NH$_3$Br</td>
</tr>
<tr>
<td>Weak</td>
<td>Weak</td>
<td>Depends on which is stronger</td>
<td>NH$_4$ClO, (NH$_4$)$_2$CO$_3$</td>
</tr>
</tbody>
</table>
Salts – Cont.

Predicting whether a salt solution will be acidic, basic or neutral:

1. Break the salt down into its cation and anion.

2. Identify (+) and (-) ions as either:
   - Spectator ion* (SI)
   - Weak acid (WA)
   - Weak base (WB)

   A spectator ion, SI, does not react with water (i.e. it does not hydrolyze) and does not change the pH of water because it is neither acidic nor basic.

3. Add the two effects to decide on effect on solution pH

Exercise: Show that Na₂CO₃ hydrolyzes in water to form a basic solution.

Work:

(1) Ionize \( \text{Na}_2\text{CO}_3 \)

\[ \text{Na}_2\text{CO}_3 \rightarrow 2\text{Na}^+ + \text{CO}_3^{2-} \]

(2) ID ions as SI, WA or WB

\( \text{Na}_2\text{CO}_3 \) \( \rightarrow \) \( \text{Na}^+ = \text{SI} \) \( \rightarrow \) \( \text{CO}_3^{2-} = \text{WB} \)

Comes from SB NaOH; no reaction with water!

(There’s no acidic H!)

Will hydrolyze to form \( \text{OH}^- \)

Hydrolysis of \( \text{CO}_3^{2-} \):

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

Base

(Will grab H+ from water)

Basic!
Exercise: Show that ammonium chloride hydrolyzes in water to form an acidic solution.

Work:

\[ \text{NH}_4\text{Cl} \quad \xrightarrow{\text{Cl}^-} \quad \text{SI} \quad \text{– comes from a strong acid, HCl} \]

**Hydrolysis of NH}_4^+:**

\[ \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+ \]

[Acidic!]

Exercise: 1) Predict whether each of the following salts will be acidic, basic or neutral in water. Show your work, including applicable hydrolysis equations.

- SrCl\(_2\)
- NaCHO\(_2\)
- AlBr\(_3\)
- NH\(_4\)NO\(_3\)
Exercise 2) Calculate the pH of each of the following aqueous solutions: (a) 0.100 M NaCHO₂, (b) 0.100 M AlBr₃ and (c) 0.100 M NH₄NO₃

WORK:
(a) pH of 0.100 M CHO₂⁻ (Na⁺ is S.I.)

W.B. = will hydrolyze to form OH⁻

\[
\text{CHO}_2^- \text{(aq)} + \text{H}_2\text{O}(l) \leftrightarrow \text{HCHO}_2 \text{(aq)} + \text{OH}^- \text{(aq)}
\]

<table>
<thead>
<tr>
<th>I</th>
<th>0.100</th>
<th></th>
<th>0</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>- x</td>
<td>+ x</td>
<td>+ x</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>(0.100 - x)</td>
<td>x</td>
<td>x</td>
<td></td>
</tr>
</tbody>
</table>

Next we **need** \(K_b\) => use \(K_a\) (HCHO₂) and \(K_w\)

Table: \(K_a\) (HCHO₂) = 1.80 \(\times\) 10⁻⁴

WORK – Cont.
(a) pH of 0.100 M CHO₂⁻

Table: \(K_b\) (CHO₂⁻) = \(\frac{1.00 \times 10^{-14}}{1.80 \times 10^{-4}}\) = 5.56 \(\times\) 10⁻¹¹

**Hydrolysis:** \(\text{CHO}_2^- \text{(aq)} + \text{H}_2\text{O}(l) \Leftrightarrow \text{HCHO}_2 \text{(aq)} + \text{OH}^- \text{(aq)}\)

\[K_b = 5.56 \times 10^{-11} = \frac{x^2}{(0.100 - x)}\] Assume \(x << 0.100\)

\[x = 2.36 \times 10^{-6} \ M = [\text{OH}^-]\]

pOH = 5.63; \(\text{pH} = 8.37\)
WORK:
(b) pH of 0.100 M AlBr₃ (Br⁻ is S.I. – comes from HBr, SA)

**Al³⁺** is a WA which exists as **Al(H₂O)₆³⁺** in water (See Kₐ table)

\[ K_a \text{ for } Al(H₂O)₆³⁺ = 1.4 \times 10^{-5} \]

**Dissociation:**
\[
Al(H₂O)₆³⁺(aq) + H₂O(ℓ) ⇌ Al(H₂O)₅(OH)³⁺(aq) + H₃O⁺(aq)
\]

\[
\begin{array}{c|c|c|c}
I & 0.100 & 0 & 0 \\
C & -x & +x & +x \\
E & (0.100 - x) & x & x
\end{array}
\]

\[
K_a = 1.4 \times 10^{-5} = \frac{x^2}{(0.100 - x)} \quad \text{Assume } x \ll 0.100
\]

\[
x = 1.18 \times 10^{-3} \quad M = [H_3O^+] \quad \text{pH} = 2.93
\]

WORK:
(c) pH of 0.100 M NH₄NO₃ (NO₃⁻ is S.I. – comes from HNO₃, SA)

**NH₄⁺** is a WA (CA of WB NH₃; From Kₐ and Kₐ table, Kₐ of NH₃ = 1.76 × 10⁻⁵)

\[
K_a (NH₄⁺) = \frac{1.00 \times 10^{-14}}{1.76 \times 10^{-5}} = 5.68 \times 10^{-10}
\]

**Ionization:**
\[
NH₄⁺(aq) + H₂O(ℓ) ⇌ NH₃(aq) + H₃O⁺(aq)
\]

\[
\begin{array}{c|c|c|c}
I & 0.100 & 0 & 0 \\
C & -x & +x & +x \\
E & (0.100 - x) & x & x
\end{array}
\]

\[
K_a = 5.68 \times 10^{-10} = \frac{x^2}{(0.100 - x)} \quad \text{Assume } x \ll 0.100
\]
\[ x = 7.54 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+] \]

\[ \text{pH} = 5.12 \]

---

**Diprotic Acids and Bases**

General formulas:

- \( \text{H}_2\text{A} \) = fully acidic form
- \( \text{HA}^- \) = intermediate form; amphoteric
- \( \text{A}^{2-} \) = fully basic or fully deprotonated form
**Equilibria involved: Diprotic Acids and Bases**

**Diprotic Acid, H$_2$A**

First dissociation: 

\[ H_2A + H_2O \rightleftharpoons \text{HA}^- + H_3O^+ \]

Second dissociation: 

\[ \text{HA}^- + H_2O \rightleftharpoons A^{2-} + H_3O^+ \]

**Dibasic species, A$^{2-}$**

First hydrolysis: 

\[ A^{2-} + H_2O \rightleftharpoons \text{HA}^- + OH^- \]

Second hydrolysis: 

\[ \text{HA}^- + H_2O \rightleftharpoons H_2A + OH^- \]

Q. How do we calculate $K_{b1}$ and $K_{b2}$ from $K_a$ values?

Note that H$_2$A and HA$^-$ species in the $K_{a1}$ expression both appear in the $K_{b2}$ expression. Similarly, the conjugates HA$^-$ and A$^{2-}$ in the $K_{a2}$ expression both appear in the $K_{b1}$ expression.

Thus,

\[ K_{a1} \cdot K_{b2} = K_w \]

\[ K_{a2} \cdot K_{b1} = K_w \]

Proof:

\[
\frac{H_2A + H_2O \xrightleftharpoons[K_{a1}]{K_{a1}} \text{HA}^- + H_3O^+}{\text{HA}^- + H_2O \xrightleftharpoons[K_{b2}]{K_{b2}} H_2A + OH^-} = \frac{2H_2O \xrightleftharpoons[K_w]{K_w} H_3O^+ + OH^-}{K_w = K_{a1} \times K_{b2}}
\]

Harris, Quantitative Chemical Analysis, 6e
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**pH Calculation: Diprotic Acids and Bases**

1. The fully acidic form, $H_2A$

   **Approximation:** In a solution of $H_2A$ (Ex. 0.050 M $H_2SO_3$), the 2nd dissociation is usually negligible that $H_2A$ behaves as a *monoprotic acid*. Also, $[A^{2-}] \approx 0$ M.

   **Calculation of pH and [species]**

   \[
   H_2A + H_2O \rightleftharpoons K_{a1} \rightarrow HA^- + H_3O^+
   \]

   Equil: \[ F-x \quad x \quad x \]

   \[ K_{a1} = \frac{x^2}{F-x} \]

---

**pH Calculation: Fully acidic form ($H_2A$) – Cont.**

**Problem 1:** Find the pH of a 0.050 M $H_2SO_3$ solution. $K_{a1} = 1.23 \times 10^{-2}; K_{a2} = 6.6 \times 10^{-8}$

\[
H_2SO_3 + H_2O \rightleftharpoons K_{a1} \rightarrow HSO_3^- + H_3O^+
\]

Equil: \[ 0.050-x \quad x \quad x \]

\[ K_{a1} = 1.23 \times 10^{-2} = \frac{x^2}{(0.050-x)} \quad x \text{ cannot be ignored since } K_{a1} \text{ isn't too small} \]

\[ x^2 + 1.23 \times 10^{-2}x - 6.15 \times 10^{-4} \quad \text{Solve for } x \text{ using quadratic equation} \]

\[ x = 1.94 \times 10^{-2}M = [H_3O^+] = [HSO_3^-] \]

\[ pH = 1.71 \]
**pH Calculations: Diprotic systems – Cont.**

2. The fully basic form, $A^{2-}$

**Approximation:** In a solution of $A^{2-}$ (Ex. 0.050 M Na$_2$SO$_3$), the 2$^{nd}$ hydrolysis is usually negligible that $A^{2-}$ behaves as a **monobasic species**. Also, [H$_2$A] ≈ 0 M.

**Calculation of pH and [species]**

\[
A^{2-} + H_2O \rightleftharpoons H A^- + OH^-
\]

Equil: \[ F-y \quad y \quad y \]

\[
K_{b1} = \frac{y^2}{F-y}
\]

pOH = -log (y) \quad \text{pH} = 14 - \text{pOH}

Recall: $K_{b1} = K_w/K_{a2}$

---

**Problem 2:** Find the pH of 0.050 N Na$_2$SO$_3$ solution:

\[
K_{a1} = 1.23 \times 10^{-2};
K_{a2} = 6.6 \times 10^{-8}
\]

**Answer:** pH = 9.94; [OH$^-$] = 8.7 x 10$^{-5}$ M
**pH Calculations:** Diprotic systems – Cont.

3. The intermediate (amphoteric) form, HA⁻
   - HA⁻ can act as an acid or a base

   **Q. What is the predominant species in a solution of HA⁻?**

   Compare $K_{a2}$ and $K_{b2}$ equilibria:

   **Dissociation:** $HA^- + H_2O \rightleftharpoons K_{a2} A^{2-} + H_3O^+$

   **Hydrolysis:** $HA^- + H_2O \rightleftharpoons K_{b2} H_2A + OH^-$

   - HA⁻ will dissociate/hydrolyze to form $A^{2-}$ and $H_2A$

   **No pH calculation involving HA⁻**

---

The intermediate form, HA⁻ (Cont.)

**Calculation of pH and [species]**

$$[H^+] \approx \sqrt{\frac{K_1 K_2 F + K_1 K_w}{K_1 + F}}$$

Where

- $K_1 = K_{a1}$
- $K_2 = K_{a2}$
- $F = F_{HA^-}$

$$pH = -\log [H^+]$$

**Quick check:** $pH = \frac{1}{2} (pK_1 + pK_2)$

- Solve for $[H_2A]$ and $[A^{2-}]$ using $[H^+]$ above and $K_1$ & $K_2$ equilibria
Trends in Acidity

1. Effect of bond strength on binary acids, HX
   - Acidity increases with decreasing bond strength (top to bottom within a group)
   - Easier to pull out H as H⁺

2. Effect of electronegativity of X in binary acids, HX
   - Acidity increases with increasing electronegativity (left to right across the table)
   - H-X bond becomes more polar; easier to pull out H⁺
**Oxyacids** = bonded to H, X and O

- **Acidity increases with increasing number of O bonded to X**

<table>
<thead>
<tr>
<th>Acid</th>
<th>Structure</th>
<th>$K_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HClO₄</td>
<td>( \text{HO} \equiv \text{Cl} \equiv \text{O} )</td>
<td>Strong</td>
</tr>
<tr>
<td>HClO₃</td>
<td>( \text{HO} \equiv \text{Cl} \equiv \text{O} )</td>
<td>1</td>
</tr>
<tr>
<td>HClO₂</td>
<td>( \text{H} \equiv \text{Cl} \equiv \text{O} )</td>
<td>(1.1 \times 10^{-2})</td>
</tr>
<tr>
<td>HClO</td>
<td>( \text{H} \equiv \text{Cl} \equiv \text{O} )</td>
<td>(2.9 \times 10^{-8})</td>
</tr>
</tbody>
</table>

Increasing acidity