Announcements

• **First Exam December 21---Christmas Break begins December 22. Silberberg Chapter 17-18, Skoog 2-7, 11-13**

• **Please keep up with the work (lots of problems in this Chapter) and see me if you have questions.**

• Mr. De Vera will have a problem-solving session on Tuesday.
Acid-Base Equilibrium

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

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

Defining \( K_a \) the acid dissociation constant at equilibrium

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

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

The magnitude of the equilibrium constant called \( K_b \) tells us how strong a base is!
Solving Acid-Base Equilibrium Problems

**Strong Acids/Bases**

100% dissociation by HA simple stoichiometry without ICE table works fine. Why?

100% dissociation means that the $[\text{H}_3\text{O}^+] = [\text{HA}]$ leading to direct calculation and no need for ICE

**Weak Acid/Bases**

ICE table as must, as we the % ionization varies with concentration of acid.

Watch for simplifications.
As the initial concentration of a weak acid (base) decreases, the percent dissociation of the acid (base) increases!
% Ionization of Monoprotic Acid

As the initial concentration of a weak acid (base) decreases, the percent dissociation of the acid (base) increases!

\[ K_a = \frac{[H_3O^+][A^-]}{[HA]} \]

\[ K_a = \frac{n_{H_3O^+} n_{A^-}}{n_{HA}} \cdot \frac{1}{V} \]
Sample Problem: Calculating pH

Calculate pH of the following solutions:

1. 0.10 M solution of NaOH

2. 0.005 M solution of calcium hydroxide: Ca(OH)$_2$

3. A solution prepared by dissolving 0.28 g of lime (CaO) in enough water to make 1.00 L limewater - Ca(OH)$_2$(aq)
Solution

1. NaOH is strong base, \([\text{OH}^-] = 0.10 \text{ M}, [\text{H}_3\text{O}^+] = 1.0 \times 10^{-13} \text{ M}, \text{ and pH 13}\)

2. Slaked lime is strong base, providing 2 OH\(^-\) per Ca\((\text{OH})_2\) unit. Therefore, \([\text{OH}^-] = 2(0.005 \text{ M}) = 0.010 \text{ M}, [\text{H}_3\text{O}^+] = 1.0 \times 10^{-12} \text{ M}, \text{ and pH 12}\)

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

3. Moles of CaO = 0.28 g x \(1 \text{ mol CaO/56.1 g} = 0.005 \text{ mol}\)

   moles OH\(^-\) produced = 0.005 mol CaO X 1 mole CaO/2mol = 0.010 mol OH\(^-\)

   Volume is 1 L, so \([\text{OH}^-] = 0.010 \text{ M}, \text{ thus pH} = 12\)
Phenylacetic acid (C₆H₅CH₂COOH, denoted as HPAc) builds up in the blood of people afflicted with phenylketonuria, an inherited genetic disorder that, if left untreated, causes mental retardation and death. A study of the acid shows that the pH of a 0.12 M solution of HPAc is 2.60. What is the $K_a$ of phenylacetic acid?

**PLAN:**

1. Write a balanced equation for acid in water.
2. Write the equation for $K_a$.
3. Set-up and fill in the ICE Table
4. Use pH, initial solution concentration and ICE table to find $K_a$. 
**SOLUTION:** What is the $K_a$ of phenylacetic acid (HPAc)?

\[
\begin{align*}
\text{HPAc}(aq) & + H_2O(l) \rightleftharpoons H_3O^+(aq) & + PAc^-(aq) \\
\text{initial} & 0.12 & - & 1 \times 10^{-7} & 0 \\
\text{change} & -x & - & +x & +x \\
\text{equilibrium} & 0.12 - x & - & x + (1 \times 10^{-7}) & x
\end{align*}
\]

\[
K_a = \frac{[H_3O^+][PAc^-]}{[HPAc]} = \frac{[x + (10^{-7})][x]}{[0.12 - x]}
\]

The pH of the solution was given: $pH = 2.6 = -\log[H_3O^+]$

Thus: $[H_3O^+] = 10^{-pH} = 10^{-2.6} = 2.5 \times 10^{-3} M = x$

Note that $2.5 \times 10^{-3} >> 10^{-7}$ (the $[H_3O^+]$ contribution from water)
\[ x \approx 2.5 \times 10^{-3} \text{ M} \approx [\text{H}_3\text{O}^+] \approx [\text{PAc}^-] \]

\[[\text{HPAc}]_{eq} = 0.12 - x = 0.12 - 2.5 \times 10^{-3} \approx 0.117 \text{ M} \]

\[ K_a = \frac{[\text{H}_3\text{O}^+][\text{PAc}^-]}{[\text{HPAc}]} = \frac{[x + (10^{-7})][x]}{[0.12 - x]} = \frac{[x][x]}{[0.12 - x]} \]

\[ K_a = \frac{(2.5 \times 10^{-3})^2}{0.117} = 5.2 \times 10^{-5} \]
The pH of a solution containing 0.250 M HF solution is 2.036. What is the value of $K_a$ for HF at equilibrium?
The pH of a solution originally containing 0.250 M HF solution is 2.036. What is the value of \( K_a \) for HF at equilibrium?

\[
\begin{align*}
\text{HF} + \text{H}_2\text{O} & \rightleftharpoons \text{H}_3\text{O}^+ + \text{F}^- \\
\text{Initial} & \quad .250 \text{ M} & \text{? M} & \text{? M} \\
\text{Change} & \quad -x \text{ M} & +x \text{ M} & +x \text{ M} \\
\text{Equilibrium} & \quad 0.250-x & x & x
\end{align*}
\]

\[
pH = 2.036 = -\log [\text{H}_3\text{O}^+] \\
K_a = \frac{[\text{H}_3\text{O}^+][\text{F}^-]}{[\text{HF}]}
\]

\[
10^{-pH} = [\text{H}_3\text{O}^+] = 10^{-2.036} = 9.2 \times 10^{-3} \text{ M}
\]

\[
[\text{HF}] = 0.25 - 0.0092 = 0.241 \text{ M}
\]

\[
K_a = (9.2 \times 10^{-3})(9.2 \times 10^{-3})/0.241 = 3.52 \times 10^{-4}
\]
Determining concentrations from $K_a$ and initial [HA]

PROBLEM:
Propanoic acid (CH$_3$CH$_2$COOH, simplified as HPr) is an organic acid whose salts are used to retard mold growth in foods. What is the [H$_3$O$^+$] of a 0.10 M aqueous solution of HPr ($K_a$ HPr = 1.3 x 10$^{-5}$)?

PLAN: Write the dissociation equation and $K_a$ expression; make assumptions about concentration that are valid; substitute.
\[
\text{HPr}^{\text{aq}} + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^{+}(aq) + \text{Pr}^{-}(aq)
\]

<table>
<thead>
<tr>
<th></th>
<th>HPr(^{aq})</th>
<th>H(_2)O(l)</th>
<th>H(_3)O(^{+})(aq)</th>
<th>Pr(^{-})(aq)</th>
</tr>
</thead>
<tbody>
<tr>
<td>initial</td>
<td>0.10</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>0.10 - x</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}_3\text{O}^{+}][\text{Pr}^{-}]}{[\text{HPr}]}
\]

\[
1.3 \times 10^{-5} = \frac{x^2}{0.10 - x}
\]

Use the quadratic formula

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]

1. If \(\frac{[\text{HA}]_{\text{initial}}}{K_a} > 100\)

Since \(K_a\) is small, we assume that \(x \ll 0.10\)
\[ K_a = 1.3 \times 10^{-5} = \frac{[H_3O^+][Pr^-]}{[HPr]} = \frac{(x)^2}{0.10} \]

\[ x = \sqrt{(0.10)(1.3 \times 10^{-5})} \]

Solving for \( x \)

\[ = 1.1 \times 10^{-3} \, M = [H_3O^+] \]

**Checking assumptions with the 5% Rule:** If \( x \) divided by initial acid concentration (or base) is < 5% then assumption is valid. It is ok because \( K_a \) is only known to within 5%!

\[ \%[HPr]_{diss} = \frac{1.1 \times 10^{-3}M}{0.10M} = 1.1\% \]

1.1% << 5% our assumption is valid and kosher
Simplifying Equilibrium Problems

IF \( \frac{[\text{HA}]_{\text{initial}}}{K_a} > 100 \) then the denominator can be reduced

Check later with the 5% rule and % dissociation

\[ \frac{[\text{H}^+]_{\text{equilibrium}}}{[\text{HA}]_{\text{initial}}} \times 100\% < 5\% \]

This is because \( K_a \) values are measured and known to about \( \pm 5\% \) accuracy. This means that our simplification of disregarding the amount disassociated can be too.
What is the pH of a 0.5 \( M \) HF solution given that \( K_a \) HF is \( 7.1 \times 10^{-4} \) (at 25\(^\circ\)C)?

1. Balanced equation for the acid + water reaction
2. Write \( K_a \) expression
3. Use ICE table to set up problem
4. Use simplifying assumptions when possible or use quadratic formula
5. Check assumption with 5% Rule
\[
\text{HF} \; (aq) \rightleftharpoons \text{H}^+ \; (aq) + \text{F}^- \; (aq)
\]

<table>
<thead>
<tr>
<th>Initial (M)</th>
<th>0.50</th>
<th>0.00</th>
<th>0.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Change (M)</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
<tr>
<td>Equilibrium (M)</td>
<td>0.50 - x</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[
K_a = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]} = 7.1 \times 10^{-4}
\]

\[
K_a = \frac{x^2}{0.50 - x} = 7.1 \times 10^{-4}
\]

\[
K_a \ll 1 \quad 0.50 - x \approx 0.50
\]

\[
K_a \approx \frac{x^2}{0.50} = 7.1 \times 10^{-4}
\]

\[
x^2 = 3.55 \times 10^{-4}
\]

\[
x = 0.019 \quad M = [\text{H}^+] = [\text{F}^-] = 0.019 \quad M
\]

\[
\text{pH} = -\log [\text{H}^+] = -\log [0.019] = 1.72 \\
[\text{HF}] = 0.50 - x = 0.48 \quad M
\]
Did my assumption pass the 5% Rule?

\[ 0.50 - x \approx 0.50 \]

When \( x \) is less than 5% of the value from which it is subtracted.

\[ x = 0.019 \quad \frac{0.019 \ M}{0.50 \ M} \times 100\% = 3.8\% \]

Less than 5%
Approximation ok.

What is the pH of a 0.05 \( M \) HF solution (at 25\(^{\circ}\)C)?

\[ K_a \approx \frac{x^2}{0.05} = 7.1 \times 10^{-4} \quad x = 0.006 \ M \]

\[ \frac{0.006 \ M}{0.05 \ M} \times 100\% = 12\% \]

More than 5%
Approximation not ok.

Must solve for \( x \) exactly using quadratic equation or method of successive approximation.