5.111 Lecture Summary #21  Wednesday, October 29, 2014

Reading for Today: Sections 11.7-11.9, 11.11-11.12 (10.7 -10.9, 10.11 – 10.12 in 4th ed.)

Topics: I. Definitions and Relationships between pK\textsubscript{w}, pH, and pOH
II. Strengths of Acids and Bases
III. Equilibrium Acid-Base Problems (Weak Acids and Weak Bases)

I. Definitions and Relationships between pK\textsubscript{w}, pH, and pOH

Autoionization of water and definition of pK\textsubscript{w}

\[
\begin{align*}
2\text{H}_2\text{O} (l) & \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq) \quad \text{or} \quad \text{H}_2\text{O} (l) + \text{H}_2\text{O} (l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq) \\
\Delta G^\circ & = +79.89 \text{ kJ/mol}
\end{align*}
\]

\[
\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{- (7.989 \times 10^4 \text{ J/mol})}{(8.3145 \text{ J/Kmol})(298.0 \text{ K})} = -32.24
\]

\[K = \text{______________} \text{ at } 298 \text{ K}\]

This very____________value indicates that only a small proportion of water molecules are ionized. Concentration of ions due to autoionization of water is very low, about 1 molecule in 200 million.

\[K = [\text{H}_3\text{O}^+][\text{OH}^-] \quad \text{This } K \text{ is called } K\text{\textsubscript{w}}.\]

Because \(K\text{\textsubscript{w}}\) is an equilibrium constant, the product of \([\text{H}_3\text{O}^+][\text{OH}^-]\) is always \(1.0 \times 10^{-14}\) at 298 K.

Note: Because the concentration of the solvent, H\textsubscript{2}O, does not change significantly in a dilute solution, it does not enter the equilibrium expression. The solvent, water, is very nearly pure, and pure liquids and pure solids are not included in equilibrium expressions.

Definitions of pH and pOH

pH Function: \[\text{pH} = -\log _____\]

pOH Function: \[\text{pOH} = -\log _____\]
Relationship between pH, pOH and pKw

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

\[ \log K_w = \log[H_3O^+] + \log[OH^-] \]

\[ -\log K_w = -\log[H_3O^+] - \log[OH^-] \]

\[ pK_w = \boxed{\text{__________} + \text{__________}} = 14.00 \text{ at } 25°C \]

II. Strength of Acids and Bases

pH of pure water  \( \text{pH} = -\log (1.0 \times 10^{-7}) = 7.00 \)

pH of an acid solution is _______________

pH of an base solution is _______________

EPA defines waste as "corrosive" if the pH is lower than 3.0 or higher than 12.5.

Demo: let’s check out the acidity or basicity of common household products.

Acid Strength

\[ \text{CH}_3\text{COOH (aq) + H}_2\text{O (l) } \rightleftharpoons H_3\text{O}^+(aq) + \text{CH}_3\text{COO}^-(aq) \]

The equilibrium constant for an acid in water is termed \( K_a \) (the acid ionization constant)

For this reaction, \( K_a = \)

The value for \( K_a \) is \( 1.76 \times 10^{-5} \text{ at } 25°C \). This small value tells us that only a small number of \( \text{CH}_3\text{COOH} \) molecules donate their proton when dissolved in water (weak acid).

Generic expressions for acids in water:

\[ \text{HA (aq) + H}_2\text{O (l) } \rightleftharpoons H_3\text{O}^+(aq) + \text{A}^-(aq) \quad \text{ACID (HA) IN WATER} \]

\[ \text{BH}^+(aq) + H_2\text{O (l) } \rightleftharpoons H_3\text{O}^+(aq) + \text{B (aq) \quad \text{ACID (BH}^+) \text{ IN WATER} } \]

A strong acid has a \( K_a >1 \) which means that the acid ionizes almost______________.

A weak acid has a \( K_a <1 \). The reaction with water does not produce many ionized species before equilibrium is reached.
pK_a = -log K_a

The lower the value of K_a, the higher the value of pK_a.
The higher the pK_a, the ________________ the acid.

A few K_a and pK_a values at 25°C

<table>
<thead>
<tr>
<th>ACID</th>
<th>K_a</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>HI</td>
<td>~10^{11}</td>
<td>~ -11</td>
</tr>
<tr>
<td>HCl</td>
<td>~10^{7}</td>
<td>~ -7</td>
</tr>
<tr>
<td>H_2SO_3</td>
<td>1.54 x 10^{-2}</td>
<td>1.81</td>
</tr>
<tr>
<td>HCOOH</td>
<td>1.77 x 10^{-4}</td>
<td>3.75</td>
</tr>
</tbody>
</table>

**Base Strength**

NH_3 (aq) + H_2O (l) ⇌ NH_4^+ (aq) + OH^- (aq)

The equilibrium constant for a base in water is termed K_b (the base ionization constant)

For this reaction, K_b =

K_b is 1.8 x 10^{-5} at 25°C. This small value tells us that only a small amount of NH_3 ionizes to NH_4^+ and OH^- in solution. A strong base reacts essentially completely to give OH^- (aq) when put in water. NH_3 is not a strong base. It is a moderately weak base.

Generic expressions for bases in water:

B (aq) + H_2O (l) ⇌ BH^+ (aq) + OH^- (aq)  BASE (B) IN WATER

A^- (aq) + H_2O (l) ⇌ HA (aq) + OH^- (aq)  BASE (A^-) IN WATER

A strong base ionizes almost completely to give OH^- in water.
pK_b = -log K_b

larger K_b, stronger base
larger pK_b, ________________ base
Strength of Conjugate Acids and Bases

The stronger the acid, the __________ its conjugate base.

The stronger the base, the __________ its conjugate acid.

Why this relationship? $K_a$ and $K_b$ are related and so are $pK_a$ and $pK_b$.

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}$$

$$\log K_a + \log K_b = \log K_w \text{ or}$$

$$pK_a + pK_b = pK_w = 14.00$$

An acid/base and its conjugate base/acid can’t both be strong.

Strong acids and bases push drive the reaction toward complete ionization:

$$\text{Strong acid } HA (aq) + H_2O (l) \rightarrow H_3O^+ (aq) + A^- (aq)$$

$$\text{Strong base } B (aq) + H_2O (l) \rightarrow BH^+ (aq) + OH^- (aq)$$

Whereas weak acids and bases are in equilibrium with their conjugates bases and acids:

$$\text{Weak acid } HA (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + A^- (aq)$$

$$\text{Weak base } B (aq) + H_2O (l) \rightleftharpoons BH^+ (aq) + OH^- (aq)$$

**III. Equilibrium Acid-Base Problems**

1. weak acid in water
2. weak base in water
3. strong acid in water
4. strong base in water
5. buffer

**Equilibrium Involving Weak Acids**

Example: Vitamin C (ascorbic acid, $\text{HC}_6\text{H}_7\text{O}_6$) has a $K_a$ of $8.0 \times 10^{-5}$. Calculate the pH of a solution made by dissolving 500. mg in 100. mL of water.

$$0.500 \text{ g} \times 1 \text{ mol} / 176.126 \text{ g} = 2.84 \times 10^{-3} \text{ mol}$$

$$2.84 \times 10^{-3} \text{ mol} / 0.100 \text{ L} = 0.0284 \text{ M}$$
\[
\text{HC}_6\text{H}_7\text{O}_6\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons \text{H}_3\text{O}^+\text{(aq)} + \text{C}_6\text{H}_7\text{O}_6^-\text{(aq)}
\]

**Initial molarity**

<table>
<thead>
<tr>
<th></th>
<th>\text{HC}_6\text{H}_7\text{O}_6</th>
<th>\text{H}_3\text{O}^+</th>
<th>\text{C}_6\text{H}_7\text{O}_6^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{molarity}</td>
<td>0.0284</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

**Change in molarity**

<table>
<thead>
<tr>
<th></th>
<th>\text{HC}_6\text{H}_7\text{O}_6</th>
<th>\text{H}_3\text{O}^+</th>
<th>\text{C}_6\text{H}_7\text{O}_6^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{molarity change}</td>
<td>-x</td>
<td>+x</td>
<td>+x</td>
</tr>
</tbody>
</table>

**Equilibrium molarity**

\[
K_a = 8.0 \times 10^{-5} = \frac{[\text{H}_3\text{O}^+][\text{C}_6\text{H}_7\text{O}_6^-]}{[\text{HC}_6\text{H}_7\text{O}_6]} = \frac{x^2}{0.0284-x}
\]

If x << 0.0284, then (0.0284-x) ~ 0.0284.

\[
K_a = 8.0 \times 10^{-5} = \frac{x^2}{0.0284}
\]

x = 0.00151 (really 2 sf, but carry extra)

Check assumption. Is 0.0284 - 0.00151 ~ 0.0284?

You can use assumption if x is less than 5% of the value in question (This 5% policy holds for any chemical equilibrium problem, not just acid-base).

Here \((0.00151/0.0284) \times 100\% = 5.3\%\) (more than 5%), so must use the quadratic equation.

This value is sometimes called the percentage ionized or percentage deprotonated.

Using quadratic eq, x = 0.00147 (really 2 sf)

\[
\text{pH} = -\log [1.47 \times 10^{-3}] =
\]

**Equilibrium Involving Weak Bases**

Example: \(\text{NH}_3\text{(aq)} + \text{H}_2\text{O}\text{(l)} \rightleftharpoons \text{NH}_4^+\text{(aq)} + \text{OH}^-\text{(aq)}\) \(K_b\) is \(1.8 \times 10^{-5}\) at 25°C.

Calculate the pH of a 0.15 M \text{NH}_3 solution at 25°C.

<table>
<thead>
<tr>
<th></th>
<th>\text{NH}_3 \text{(aq)}</th>
<th>\text{NH}_4^+ \text{(aq)}</th>
<th>\text{OH}^- \text{(aq)}</th>
</tr>
</thead>
<tbody>
<tr>
<td>\text{molarity}</td>
<td>0.15</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

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5
Base ionization \( K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \) constant

Using assumption, \( x = 0.00164 \)

Check assumption:

\[
p\text{OH} = -\log [\text{OH}^-] = -\log [0.00164] = 2.79
\]

\[
\text{pH} =
\]