**5.111 Lecture Summary #21**                                    **Wednesday, October 29, 2014**
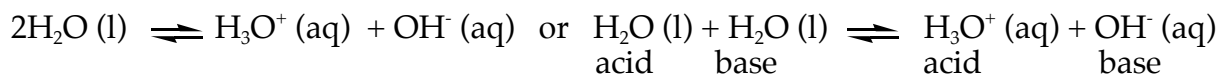
**Reading for Today**: Sections 11.7-11.9, 11.11-11.12 (10.7 -10.9, 10.11 – 10.12 in 4$^{th}$ ed.)
**Reading for Lecture #22**:  Sections 11.13, 11.18-11.19, 12.1-12.3 (10.13, 10.18-10.19, 11.1-11.3 in 4$^{th}$ ed.)
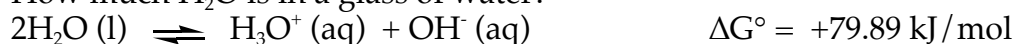
**Topics**: I. Definitions and Relationships between $pK_w$, pH, and pOH
         II. Strengths of Acids and Bases
         III. Equilibrium Acid-Base Problems (Weak Acids and Weak Bases)


**I. Definitions and Relationships between $pK_w$, pH, and pOH**

Autoionization of water and definition of $pK_w$

$2H_2O$ (l)  $\rightleftharpoons$ $H_3O^+$ (aq)  + $OH^-$ (aq)  or  $H_2O$ (l) + $H_2O$ (l)  $\rightleftharpoons$  $H_3O^+$ (aq) + $OH^-$ (aq)
                                                                    acid       base                    acid           base

How much $H_2O$ is in a glass of water?
$2H_2O$ (l)  $\rightleftharpoons$   $H_3O^+$ (aq)  + $OH^-$ (aq)                    $\Delta G° =$  +79.89 kJ/mol


$$\ln K \; = \; -\Delta G°/RT \; = \; \frac{- ( \, 7.989 \text{ x } 10^4 \text{ J/mol})}{(8.3145 \text{ J/Kmol})(298.0 \text{ K})} \; = \; -32.24$$


K = _____ at 298 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 = $[H_3O^+][OH^-]$            This K is called $K_w$.

**Because $K_w$ is an equilibrium constant, the product of $[H_3O^+][OH^-]$ is always 1.0 x 10$^{-14}$ at 298 K**.

*Note: Because the concentration of the solvent, $H_2O$, 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:            pH  = -log _____

pOH Function:          pOH = -log _____

Relationship between pH, pOH and $pK_w$

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

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

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

$$pK_w = \underline{\hspace{1.5cm}} + \underline{\hspace{1.5cm}} = 14.00 \text{ at } 25°C$$

| $[H_3O^+]$ | pH | |
|---|---|---|
| 10 | -1 | ACIDIC |
| 1 | 0 | |
| $10^{-1}$ | 1 | |
| $10^{-2}$ | 2 | corrosive |
| $10^{-3}$ | 3 | |
| $10^{-4}$ | 4 | |
| $10^{-5}$ | 5 | |
| $10^{-6}$ | 6 | |
| $10^{-7}$ | 7 | NEUTRAL |
| $10^{-8}$ | 8 | |
| $10^{-9}$ | 9 | |
| $10^{-10}$ | 10 | |
| $10^{-11}$ | 11 | |
| $10^{-12}$ | 12 | corrosive |
| $10^{-13}$ | 13 | BASIC |
| $10^{-14}$ | 14 | |
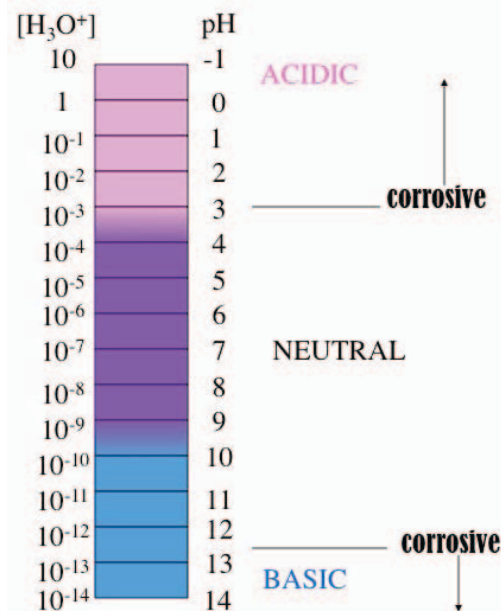
## II. Strength of Acids and Bases

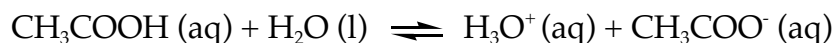pH of pure water  $pH = -\log(1.0 \times 10^{-7}) = 7.00$

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.
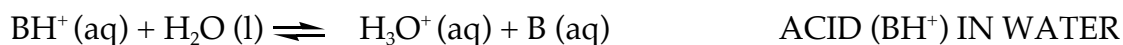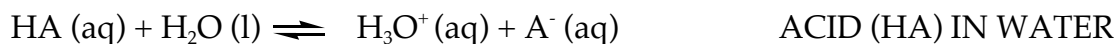
Acid Strength

$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3COO^-\ (aq)$

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 $1.76 \times 10^{-5}$ at 25°C.  This small value tells us that only a small number of $CH_3COOH$ molecules donate their proton when dissolved in water (weak acid).

Generic expressions for acids in water:

$HA\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$          ACID (HA) IN WATER

$BH^+\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + B\ (aq)$          ACID (BH$^+$) 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.
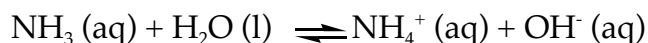
$pK_a = -\log K_a$

The lower the value of $K_a$, the higher the value of $pK_a$.

The higher the $pK_a$. "ij g"‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾‾"ij g"cekf 0

A few $K_a$ and $pK_a$ values at 25°C

| ACID | $K_a$ | $pK_a$ |
|------|-------|--------|
| HI | $\sim 10^{11}$ | $\sim -11$ |
| HCl | $\sim 10^{7}$ | $\sim -7$ |
| $H_2SO_3$ | $1.54 \times 10^{-2}$ | 1.81 |
| HCOOH | $1.77 \times 10^{-4}$ | 3.75 |

Base Strength

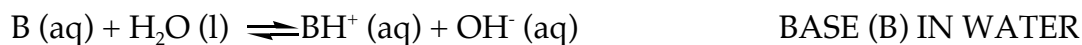$NH_3$ (aq) + $H_2O$ (l) $\rightleftharpoons$ $NH_4^+$ (aq) + $OH^-$ (aq)

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

For this reaction, $K_b$ =

$K_b$ is $1.8 \times 10^{-5}$ 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) $\rightleftharpoons$ $BH^+$ (aq) + $OH^-$ (aq)          BASE (B) IN WATER

$A^-$ (aq) + $H_2O$ (l) $\rightleftharpoons$ HA (aq) + $OH^-$ (aq)          BASE ($A^-$) IN WATER
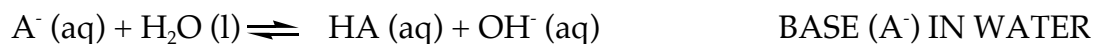
A strong base ionizes almost completely to give $OH^-$ in water.

$pK_b = -\log K_b$

larger $K_b$, stronger base

larger $pK_b$. ‾‾‾‾‾‾‾‾‾‾‾‾‾‾"dcug

<u>Strength of Conjugate Acids and Bases</u>

The stronger the acid, the
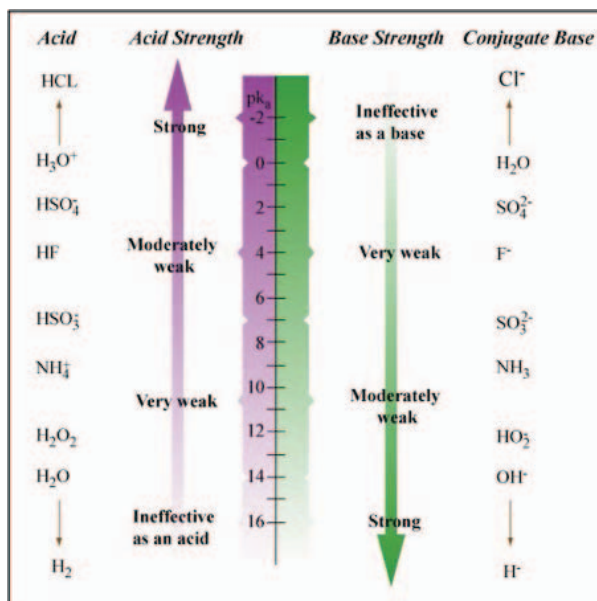_____ its conjugate base.

The stronger the base, the
_____its conjugate acid.

Why this relationship? $K_a$ and $K_b$ are
related and so are $pK_a$ and $pK_b$.
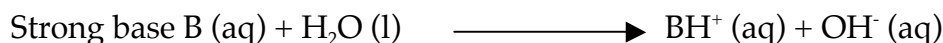
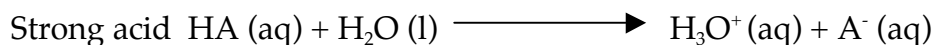$$K_a \times K_b \;=\; K_w \;=\; 1.0 \times 10^{-14}$$

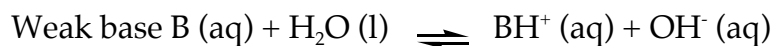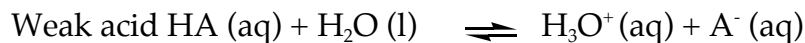$$\log K_a + \log K_b = \log K_w \;\; \text{or}$$

$$pK_a + pK_b = pK_w = 14.00$$

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

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

Strong acid  HA (aq) + $H_2O$ (l) $\longrightarrow$ $H_3O^+$ (aq) + $A^-$ (aq)

Strong base B (aq) + $H_2O$ (l) $\longrightarrow$ $BH^+$ (aq) + $OH^-$ (aq)

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

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

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

**III. Equilibrium Acid-Base Problems**
1. weak acid in water $\rightleftharpoons$ salt in water
2. weak base in water
3. strong acid in water
4. strong base in water
5. buffer

<u>Equilibrium Involving Weak Acids</u>

Example: Vitamin C (ascorbic acid, $HC_6H_7O_6$) 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 g x 1 mol/176.126 g = $2.84 \times 10^{-3}$ mol

$2.84 \times 10^{-3}$ mol/0.100 L = 0.0284 M

$HC_6H_7O_6 (aq) + H_2O (l) \rightleftharpoons H_3O^+ (aq) + C_6H_7O_6^- (aq)$
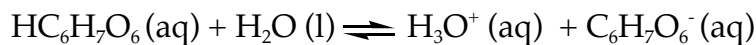
|  | $HC_6H_7O_6$ | $H_3O^+$ | $C_6H_7O_6^-$ |
|---|---|---|---|
| initial molarity | 0.0284 | 0 | 0 |
| change in molarity | -x | +x | +x |
| equilibrium molarity |  |  |  |

$$K_a = 8.0 \times 10^{-5} = \frac{[H_3O^+][C_6H_7O_6^-]}{[HC_6H_7O_6]} = \frac{x^2}{0.0284 - x}$$

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) x 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)

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

Equilibrium Involving Weak Bases

Example: $NH_3 (aq) + H_2O (l) \rightleftharpoons NH_4^+ (aq) + OH^- (aq)$      $K_b$ is $1.8 \times 10^{-5}$ at 25°C.

Calculate the pH of a 0.15 M $NH_3$ solution at 25°C.

|  | $NH_3 (aq)$ | $\rightleftharpoons$ | $NH_4^+ (aq)$ + | $OH^- (aq)$ |
|---|---|---|---|---|
| initial molarity | 0.15 |  | 0 | 0 |
| change in molarity |  |  |  |  |
| equilibrium molarity |  |  |  |  |

base
ionization ($K_b$) = $\dfrac{[NH_4^+][OH^-]}{[NH_3]}$ =    Using assumption, x= 0.00164
constant

Check assumption:

pOH = -log [OH-] = -log [0.00164] = 2.79

pH =

5.111 Principles of Chemical Science
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