**5.111 Lecture Summary #22** **Wednesday, October 31, 2014**

**Reading for Today**: Sections 11.13, 11.18-11.19, 12.1-12.3 in 5th ed. (10.13, 10.18-10.19, 11.1-11.3 in 4th ed.)
**Reading for Lecture #23**: Sections 12.4-12.6 in 5th ed. (4th ed: 11.4-11.6)

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**Topics**: I. pH of salt solutions
II. Buffers!

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## I. pH of salt solutions

A salt is formed by the neutralization of an acid by a base.

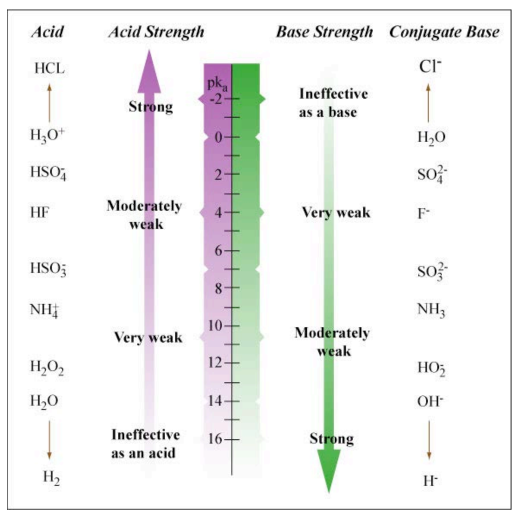
HCl + NaOH gives NaCl and $H_2O$

The pH of salt in water is not always ___________________.

Salts that contain the conjugate acids of weak bases produce *acidic* aqueous solutions; so do salts that contain small, highly charged metal cations (e.g. $Fe^{3+}$).

(Note: all Group 1 and 2 metals (e.g. $Li^+$, $Ca^{+2}$) and all metal cations with charge +1 (e.g. $Ag^{+1}$) are *neutral*.)

Salts that contain the conjugate bases of weak acids produce *basic* aqueous solution.




1) $NH_4Cl$ (aq) will produce a(n) _______________ solution.

$NH_4^+$ Is $NH_4^+$ a conjugate acid of a weak base and therefore a weak acid? $K_a = 5.6 \times 10^{-10}$

Is $NH_3$ a weak base? $K_b = 1.8 \times 10^{-5}$

$Cl^-$ Is $Cl^-$ a conjugate base of a weak acid and therefore a weak base?

Is HCl a weak acid? $K_a = 10^7$

2) $NaCH_3COO$ (aq) will produce a(n) ________________ solution. $K_a$ of $CH_3COOH$ is $1.76 \times 10^{-5}$

$Na^+$ Is $Na^+$ a conjugate acid of a weak base and therefore acidic?

$CH_3COO^-$ Is $CH_3COO^-$ a conjugate base of a weak acid and therefore basic?
Is $CH_3COOH$ is weak acid?

3) General rule for compound XY

| | | |
|---|---|---|
| $X^+$ | Is $X^+$ a conjugate acid of a weak base? | If yes, then acidic; If no, neutral |
| $Y^-$ | Is $Y^-$ a conjugate base of a weak acid? | If yes, then basic; If no, neutral |

Overall: acidic+neutral=acidic; basic+neutral=basic;neutral+neutral=neutral

**II. BUFFERS!**

A **buffer** solution is any solution that maintains an approximately ________________pH despite small additions of acid and base.

An **acid buffer**: consists of a _____________and its __________________ supplied as a salt. It buffers on the acidic side of neutral.

A **base buffer**: consists of a weak **base** and its conjugate **acid** supplied as a salt. It buffers on the basic side of neutral.

Acid Buffer Example: Mix acetic acid with an acetate salt and get dynamic equilibrium:

$CH_3COOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + CH_3CO_2^-\ (aq)$

What happens if strong acid is added to a solution containing approximately equal amounts of $CH_3CO_2^-$ and $CH_3COOH$?

- __________________ reaction
- The added $H_3O^+$ ions are effectively_____________ and the pH stays constant.

What happens if $OH^-$ base is added?

- The base removes a proton from $CH_3COOH$ to form $H_2O$ and $CH_3CO_2^-$ molecules.
- The added ________ ions are effectively removed and the pH stays constant.

**Acid buffer action**: The weak acid, HA, transfers protons to $OH^-$ ions supplied by strong base. The conjugate base, $A^-$, of the weak acid accepts protons from the $H_3O^+$ ions supplied by a strong acid.

A strong acid and the salt of its conjugate base don't make a good buffer. Why?

Base Buffer Example: $NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$

When strong acid is added, $NH_3$ accepts protons from incoming acid to make $NH_4^+$. When strong base is added, $NH_4^+$ donates a proton to form $NH_3$ and $H_2O$.

pH remains the _________ .

**Base buffer action**: The weak base, B, accepts protons supplied by strong acid.
The conjugate acid, $BH^+$, of the weak base transfers protons to the $OH^-$ ions supplied by a strong base.

**A buffer is a mixture of weak conjugate acids and bases that stabilize the pH of a solution by providing a _______________ or ________________ for protons.**

<u>Buffers are important in biology!</u> Blood is buffered in the range of 7.35-7.45. Buffering agents: $H_2CO_3/HCO_3^-$

<u>Sample Buffer Problem</u>: Suppose 1.00 mol of HCOOH and 0.500 mol of NaHCOO are added to water and diluted to 1.0 L. Calculate the pH. ($K_a = 1.77 \times 10^{-4}$)

| | $HCOOH + H_2O \rightleftharpoons$ | $H_3O^+$ | $+ HCOO^-$ |
|---|---|---|---|
| initial molarity | 1.00 | 0 | 0.500 |
| change in molarity | -x | +x | +x |
| equilibrium molarity | | | |

$K_a = 1.77 \times 10^{-4} =$

Using approximation that x is small compared to 1.00 and 0.500,

$K_a = 1.77 \times 10^{-4} =$

$x = 3.54 \times 10^{-4}$ M

Check assumption

$3.54 \times 10^{-4} =$

**pH** =

<u>Now –Calculate the pH given that 0.100 mol of a strong acid (HCl) had been included in the 1.0 L solution.</u>

Because 0.100 mol of HCl reacts with ____________ number of moles of $HCOO^-$ to form ____________ moles of HCOOH:

For $HCOO^-$, 0.500 mol - 0.100 mol = ___________ mol $[HCOO^-]$ = 0.400 mol/1.0 L =0.400 M

For HCOOH, 1.00 mol + 0.100 mol = ___________ mol [HCOOH] = 1.10 mol/1.0 L =1.10 M

| | $HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$ |
|---|---|
| initial molarity | |
| change in molarity | |
| equilibrium molarity | |

$K_a = 1.77 \times 10^{-4} =$

Using approximation that x is small,

$K_a = 1.77 \times 10^{-4} =$ $x = 4.87 \times 10^{-4}$

Check assumption (5% rule)

$pH = -\log [H_3O^+] = 3.31$

So addition of 0.10 mol of strong acid only changed pH from 3.45 to 3.31!

Designing a Buffer

One must consider the relationship between the ratio of [HA] to [A$^-$], p$K_a$, and pH in designing a buffer.

$HA\ (aq) + H_2O \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq)$ $$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearrange: $$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

Take logarithms of both sides: $$\log [H_3O^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

Multiply by (-) : $$-\log [H_3O^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$

That is: $$pH = pK_a - \log \left( \frac{[HA]}{[A^-]} \right)_{eq}$$

The values of [HA] and [A$^-$] in the equation are at equilibrium.

However, a weak acid HA typically loses only a tiny fraction of its protons.

Likewise, a weak base A- typically only accepts a tiny fraction of protons.

So initial concentration is approximately ________________ to equilibrium concentration

| |
|---|
| So $pH \cong pK_a - \log\left(\frac{[HA]_0}{[A^-]_0}\right)$ Henderson-Hasselbalch Equation<br>↖ initial |

This assumption is valid when $[H_3O^+]$ is ____________ compared to [HA] and $[A^-]$ (i.e. less than 5%).

Example: Design a buffer system with pH 4.60.

Acetic acid is suitable with a $pK_a$ of 4.75

**A buffer solution is most effective in the range of $pK_a$ ±1**

$$pH = pK_a - \log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0}$$

$$\log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = pK_a - pH = 4.75 - 4.60 = 0.15$$

$$\frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = 10^{0.15} = 1.4$$

The ratio is more important than the amounts used.

However, the amounts do affect the capacity of the buffer to __________________ changes in pH. Higher concentrations = more resistance to change.

If you use too low concentrations, the Henderson-Hasselbalch equation won't be valid.

For pH 4.60, $[H_3O^+]$ is $2.5 \times 10^{-5}$.

$$\frac{2.5 \times 10^{-5}}{[HA] \text{ or } [A-]} \times 100\% < 5\%$$

need concentration > $5.0 \times 10^{-4}$ M