CHE 2060: Guide to using the Henderson-Hasselbalch equation

Biological organism and solutions are **buffered**, meaning that they are able to maintain a stable pH when challenged by addition of acid or base. When added to unbuffered solutions, acid would cause the pH to drop while base would cause the pH to increase. **Buffered solutions contain a weak acid and a salt of that weak acid.** The acid provides protons to counter any base added to the buffered solution. The salt of the weak acid is a metal cation ionically bound to the anion of the weak salt and that anion counters (or absorbs) the protons of any acid added to the buffered solution. Weak acids create good buffers for pH values close to their **pKa values**.

The **Henderson-Hasselbalch equation** describes the relationship between:
- The pH of the buffered solution;
- The pKa value of the weak acid; and
- The ratio of the weak acid to its conjugate base (aka its salt).

$$pH = pKa + \log \frac{[\text{conjugate base}]}{[\text{weak acid}]}$$

The Henderson-Hasselbalch equation can be **rearranged** to solve for any of its components. Here are a few **reminders or pointers**.
- To solve for the log of a ratio, take the anti-log of both sides of the equation.
- To take an antilog use the appropriate button on your calculator or raise 10 to the power of the value to calculate that value's antilog.

Functional groups are the parts of organic molecules that do work by participating in chemical reactions. For many functional groups, their **protonation** – and thus reactivity – is dependent on the pH of their environment, or solution. For example, carboxylic acid groups are protonated and act as acids only at pH values below their pKa of 4.7ish. Far above that pH carboxylic acids become deprotonated carboxylate ions and act as bases.
- **When the pH of a functional group's environment is close to that group's pKa roughly half of the functional groups are protonated, and half are unprotonated.**

See examples and solutions on the next page……………
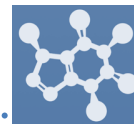
Examples:

A. A buffer is made with 30 mM acetic acid (pKa 4.76) and 40 mM sodium acetate. What is the pH of the buffer?

pH = pKa + log (40 mM/30 mM) = 4.76 + 0.125 = 4.88

B. A protein with exposed aspartic acid side chains is placed in a solution with a pH of 7.0. What percentage of the aspartic acid side chains are protonated? Use the Henderson-Hasselbalch equation!

7.0 = 4.76 + log [carboxylate ion]   →   2.24 = log [carboxylate ion]
             [carboxylic acid]   [carboxylic acid]

To solve, take the antilog of both sides (see reminders or pointers above).

$10^{(2.24)}$ = [carboxylate ion]   →   174:1   →   (174/175)(100) = 99.5% deprotonated
             [carboxylic acid]

C. How much sodium formate do you need to add to 400 mL of 1.00 M formic acid to make a buffer with pH 3.50?
(MW sodium formate is 68.01; Ka of formic acid is 1.77 E-4).

pKa = - log (1.77 E-4) = 3.75

3.50 = (-log 1.77 E-4) + log [sodium formate]   → - 0.25 = log [sodium formate]
                              [1.00]

To solve, take the antilog of both sides → $10^{-0.25}$ = [sodium formate] = 0.562 M

0.400 L   0.562 mol   68.01 g = 15.29 g of sodium formate
               1 L   1 mol

D. Aspirin (acetylsalicylic acid) has a pKa of 3.4. What is the ratio of anion/weak acid in ___?
(a) blood, pH 7.4
(b) stomach acid, pH 1.4

(a) 7.4 = 3.4 + log (anion/weak acid) → 4.0 = log (anion/weak acid) → $10^{4.0}$ = 1 E4 !!!
                                                    So, 10,000 are deprotonated for every 1 protonated.

(b) 1.4 = 3.4 + log (anion/weak acid) → - 2.0 = log (anion/weak acid) → $10^{-2.0}$ = 0.01
                                                    So, only 1 is deprotonated for every 100 protonated.