

Homework 2: Chapter 2 1, 2, 4, 9, 16, 20, 27, 28, 31, 35

① The hydroxyl group of ethanol can form hydrogen bonds with the water molecules. The ethanol would be trapped in clathrate cages, so it associates with other ethanol molecules due to the hydrophobic effect

- ② a) $\text{pH} = -\log [\text{H}^+] = 4.75$
b) $\text{pH} = 9.19$
c) $\text{pH} = 4$
d) $\text{pH} = 4.82$

④ 10.0ml of acid
7.7ml of 0.1mole/L NaOH

a) Find the # of moles of OH^- it took to neutralize the acid in the stomach solution.
Since stomach acid is HCl , the chemical rxn is



For every 1 mole of OH^- added, 1 mole of H^+ is consumed. This means that the # of moles of OH^- used equals the # of moles of H^+ in the sample.

$$0.0077 \text{ L} \times \frac{0.1 \text{ mole H}^+}{\text{L}}, \quad 7.7 \times 10^{-4} \text{ moles OH}^- \times \frac{1 \text{ mole H}^+}{1 \text{ mole OH}^-}$$

7.2×10^{-4} moles of H^+ in the sample.

The sample was 10 ml, so the molarity of H^+ in the sample was:

$$\frac{7.2 \times 10^{-4} \text{ moles } H^+}{0.010 \text{ L}} = 0.072 \text{ M } H^+$$

$$pH = -\log [H^+] = -\log (0.072)$$

$$pH = 1.14$$

- 9) a) A strong acid has a greater tendency to lose its protons
b) The strongest acid in the world has a K_a of ∞ , so it has a higher K_a than a weak acid
c) The strong acid has a much lower pK_a than the weak acid.

16) $0.12 \text{ M } NH_4Cl$ and $0.03 \text{ M } NaOH$
 pK_a of NH_4^+/NH_3 is 9.25



Remember NH_4^+ is a weak acid, so not very much NH_3 or H_3O^+ will be made.

However, having $0.03M OH^-$ present is significant. Every H_3O^+ that is made when NH_4^+ dissociates is reacted away, so more NH_4^+ dissociates.

We know that $0.03M NH_3$ is made because of the OH^-/H_3O^+ reaction pulling more and more NH_4^+ apart into NH_3 and H_3O^+ . Since $0.03M H_3O^+$ was reacted, $0.03M NH_3$ had to be made.

The sum total of the NH_4^+ and NH_3 species has to be $0.12M$, so the following must be true

$$[NH_4^+] + [NH_3] = 0.12M$$

$$[NH_4^+] + (0.03M) = 0.12M$$

$$[NH_4^+] = 0.09M$$

Use the Henderson-Hasselbalch equation to determine the pH.

$$pH = pK_a + \log \left(\frac{[Base]}{[Acid]} \right)$$

$$= 9.25 + \log \left(\frac{[NH_3]}{[NH_4^+]} \right)$$

$$= 9.25 + \log \left(\frac{0.03}{0.09} \right)$$

$$\boxed{pH = 8.77}$$

20) 0.1 L of 0.1 M histidine @ pH 5.4

Titrate with 0.04 L of 0.1 M HCl
What is final pH?

- a) Use the Henderson-Hasselbalch equation to determine the initial amounts of species in the buffer. But what pK_a should be used? The one closest to the buffer pH. Be certain that you understand why. Since the pH is 5.4, we are only worried about species 2 and 3
 $pK_a = 6.0$

$$pH = pK_a + \log \left(\frac{[His]}{[HisH^+]} \right)$$

$$5.4 = 6.0 + \log \left(\frac{[His]}{[HisH^+]} \right)$$

$$\log \left(\frac{[His]}{[HisH^+]} \right) = -0.6$$

$$\frac{[His]}{[HisH^+]} = 10^{-0.6} \quad \text{or} \quad \frac{[His]}{[HisH^+]} = 0.25$$

$$\frac{[HisH^+]}{[His]} = \frac{4}{1}$$

or

This ratio of 4 molecules of HisH^+ to every 1 His is important b/c we can use it to calculate the molarity of each species.

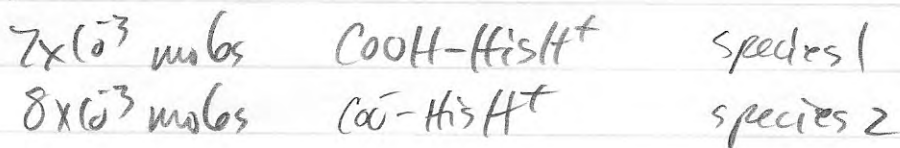
There are 5 total His molecules in the ratio, 4 HisH^+ and 1 His . We can divide the molarity by 5 to get the amounts of each species.

$$\frac{0.1 \text{ M}}{5} = 0.02 \text{ M} \quad \text{so the molarities of each are:}$$

$$\begin{aligned} 0.08 \text{ M } \text{HisH}^+ &\times 0.1 \text{ L} = 8 \times 10^{-3} \text{ moles } \text{HisH}^+ \\ 0.02 \text{ M } \text{His} &\times 0.1 \text{ L} = 2 \times 10^{-3} \text{ moles } \text{His} \end{aligned}$$

We are adding 0.04 L of 0.1 M HCl, a strong acid. This equates to 4×10^{-3} moles of H^+ added.

The H^+ will react with the His to form HisH^+ . We will still have 2×10^{-3} moles of H^+ left, so we end up making 2×10^{-3} moles of COOH-HisH^+ (species 1) from species 2. This leaves us with:



We now have 140 ml of solution, so the molarities are

$$\frac{2.0 \times 10^{-3} \text{ moles COOH-HisH}^+}{0.140 \text{ L}}, \quad 0.014 \text{ M COOH-HisH}^+$$

$$\frac{8 \times 10^{-3} \text{ moles COO}^- \text{-HisH}^+}{0.140 \text{ L}}, \quad 0.057 \text{ M COO}^- \text{-HisH}^+$$

Using the Henderson Hasselbach equation at pK_1 (why pK_1 ? Because we forced the species to be species 1 or species 2, so we had to work @ the new K_1 that described the new equilibrium.

$$pH = 1.8 + \log \left(\frac{[0.057]}{[0.014]} \right)$$

$$pH = 1.8 + 0.61$$

$$\boxed{pH = 2.41}$$



(27)

0.01 mole Lactic acid

L

0.05 mole Lactate

L

$pK_a = 3.86$

$$a) \text{pH} = pK_a + \log \left(\frac{[\text{Lactate}]}{[\text{Lactic Acid}]} \right)$$

$$\text{pH} = 3.86 + \log \left(\frac{0.05 \text{ M}}{0.01 \text{ M}} \right)$$

$\text{pH} = 4.56$

This makes sense since there is more of conjugate base (lactate) than the acid.

b) 5 mL of 0.5 M HCl

$$0.005 \text{ L} \times \underline{0.5 \text{ mole H}^+}, \quad 2.5 \times 10^{-3} \text{ moles H}^+$$

L

These will react with lactate to create lactic acid in the reaction:



We'll take away 2.5×10^{-3} moles of lactate to form 2.5×10^{-3} moles of lactic acid, so we need the # of moles of each at the start of the titration.

$$\frac{0.05 \text{ moles lactate}}{1 \text{ L}} \times 1 \text{ L} = 0.05 \text{ moles lactate}$$

$$\frac{0.01 \text{ moles lactic acid}}{1 \text{ L}} \times 1 \text{ L} = 0.01 \text{ moles lactic acid}$$

We are adding: $0.005 \text{ L} + \frac{0.5 \text{ moles H}^+}{\text{L}}$, $7.5 \times 10^{-3} \text{ moles H}^+$

The added H^+ will convert the lactate to lactic acid, so we will have

$$0.05 \text{ moles lactate} - 7.5 \times 10^{-3} \text{ moles} = 0.0475 \text{ moles lactate left}$$

$$0.01 \text{ moles lactic acid} + 7.5 \times 10^{-3} \text{ moles} = 0.0175 \text{ moles lactic acid}$$

Both are in 1.005 L , so the new molarities are:
lactate: $0.0475 / 1.005 \text{ L} = 0.0473 \text{ M}$ lactate
lactic acid: $0.0175 \text{ moles} / 1.005 \text{ L} = 0.0174 \text{ M}$ lactic acid

The pH is:

$$\text{pH} = \text{pK}_a + \log \left(\frac{[\text{lactate}]}{[\text{lactic acid}]} \right) = 3.86 + \log \left(\frac{0.0473}{0.0175} \right)$$

$$\text{pH} \approx 4.43 \quad \text{or a difference of } \approx \boxed{0.1 \text{ pH units}}$$

c) Having 2.5×10^{-3} moles H^+ of pure water
 1×10^{-7} mole H^+ in pure water

$$\frac{2.5 \times 10^{-3} \text{ moles } H^+ \text{ added}}{1.005 \text{ L total volume}} = 2.49 \times 10^{-3} \text{ M } H^+$$

$$pH = -\log(2.49 \times 10^{-3} \text{ M})$$

$$pH = 2.60$$

Re pH change would be

$$7 - 2.60 = 4.39 \text{ pH units}$$

(28) pH of $0.2 \text{ M NaCH}_3\text{COO}$ $0.6 \text{ M CH}_3\text{COOH}$

$$pH = pK_a + \log \left(\frac{[CH_3COO^-]}{[CH_3COOH]} \right)$$

$$pH = 4.76 + \log \left(\frac{0.2 \text{ M}}{0.6 \text{ M}} \right)$$

$$pH = 4.28$$

21) X has COOH w/ $pK_a = 2.0$

has unk. group w/ pK_a b/w 5 and 8
What is @ start?

0.1M X @ pH 2 100mL

The $pH = pK_a$, so we know that 0.05M $COOH-X-RH$
0.05M COO^-X-RH
are present in solution

What happens?

We add 75mL of 0.1M NaOH and the pH increases to 6.72.

$$pH = pK_a + \log \left(\frac{[COO^-X-R^-]}{[COO^-X-RH]} \right)$$

we are now in the
unknown group's ionization
range.
 $COO^-X-RH \rightleftharpoons COO^-X-R^-$

But how much of everything (COO^-X-RH and COO^-X-R^-)
do we have?

The amount of X can't change and we know
we converted all species 1 to species 2 with the first
part of the OH⁻ added, then we converted species 2 to
species 3 (COO^-X-R^-) with the rest. So let's find
the # of moles of species 1, species 2 and OH⁻ we
start with...

$$0.11 \text{ L} \times \frac{0.05 \text{ mole}}{\text{L}} \text{COOH-X-RH} , \quad 5 \times 10^{-3} \text{ moles COOH-X-RH}$$

$$0.11 \text{ L} \times \frac{0.05 \text{ mole}}{\text{L}} \text{COO}^- \text{-X-RH} , \quad 5 \times 10^{-3} \text{ moles COO}^- \text{-X-RH}$$

$$0.075 \text{ L} \times \frac{0.1 \text{ mole}}{\text{L}} \text{OH}^- , \quad 7.5 \times 10^{-3} \text{ moles OH}^-$$

We react all 5×10^{-3} moles COOH-X-RH with 5×10^{-3} moles of OH^- to make another 5×10^{-3} moles of $\text{COO}^- \text{-X-RH}$, so now we have:

$$1 \times 10^{-2} \text{ moles COO}^- \text{-X-RH} \quad \text{and} \\ 2.5 \times 10^{-3} \text{ moles OH}^- \quad \text{left}$$

The OH^- reacts off 2.5×10^{-3} moles of $\text{COO}^- \text{-X-RH}$ to form $\text{COO}^- \text{-X-R}^-$. Now we have:

$$7.5 \times 10^{-3} \text{ moles COO}^- \text{-X-RH} \quad \text{in the 175 mL} \\ 2.5 \times 10^{-3} \text{ moles COO}^- \text{-X-R}^-$$

Plug into the Henderson-Hasselbalch equation to get:

$$\text{pH} = \text{pK}_A + \log \left(\frac{2.5 \times 10^{-3} \text{ moles COO}^- \text{-X-R}^- / 0.175 \text{ L}}{7.5 \times 10^{-3} \text{ moles COO}^- \text{-X-RH} / 0.175 \text{ L}} \right)$$

$$6.72 = pK_A + \log(0.33)$$

$$pK_A = 7.20$$

(35) The bicarbonate buffer system is:



If more and more CO_2 builds up in the bloodstream then by Le Chatelier's principle, more H^+ should be formed.

More H^+ means a lower pH.

SELF-TEST

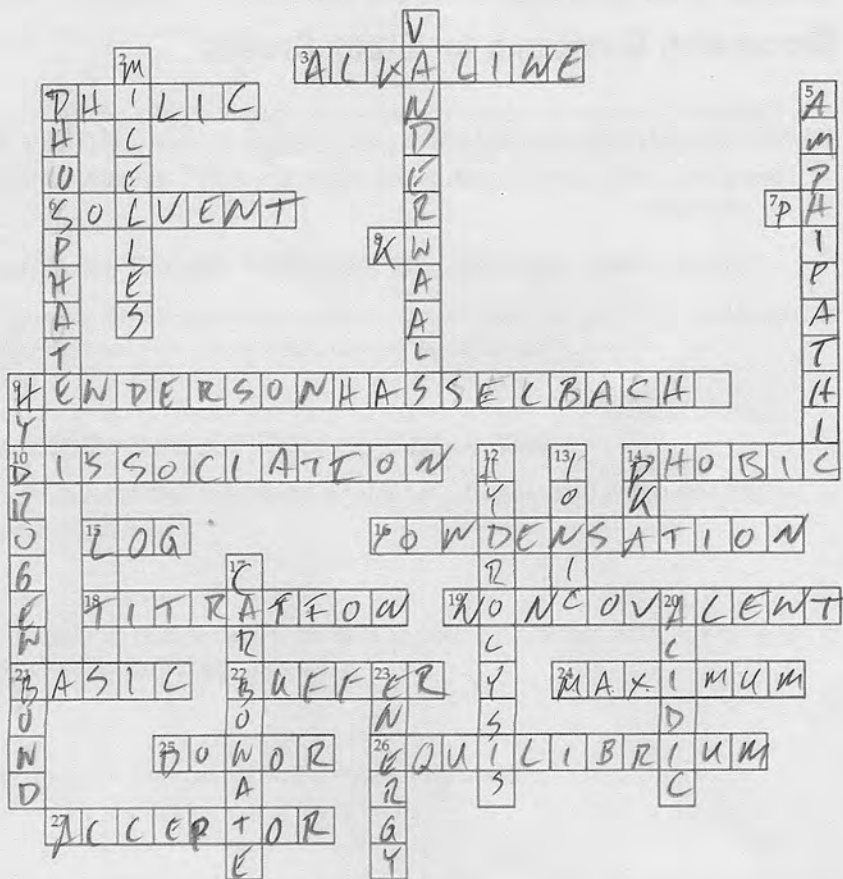
Do You Know the Terms?

ACROSS

- Describes a solution with a $[H^+]$ of 1×10^{-8} .
- Hydro _____ molecules can form energetically favorable interactions with water molecules.
- Water is often referred to as the "universal _____" because of its ability to hydrate molecules and screen charges.
- Denotes the concentration of H^+ (and therefore of OH^-) in an aqueous solution.
- The ion product of water; it is 1×10^{-14} M in aqueous solutions at 25 °C.
- The _____ equation; describes the relationship between pH and the pK_a of a buffer.
- The equilibrium constant for the reaction $HA \rightleftharpoons H^+ + A^-$ is also called the _____ constant, K_a .
- Hydro _____ molecules decrease the entropy of an aqueous system by causing water molecules to become more ordered.
- The numbers 1, 10, 100, and 1000 are placed at equal intervals on a _____ scale.
- Reaction in which two reactants combine to form a single product with the elimination water.
- A plot of pH vs. OH^- equivalents added is a _____ curve.
- Weak interactions that are crucial to the structure and function of macromolecules.
- Describes a solution in which $[OH^-]$ is greater than $[H^+]$.
- A mixture of a weak acid and its conjugate base.
- Enzymes show maximum activity at a characteristic pH _____.
- HA is a proton _____.
- The point in a reversible chemical reaction at which the rate of product formation equals the rate of product breakdown to the starting reactants.
- A^- is a proton _____.

DOWN

- The _____ radius is approximately twice the distance of a covalent radius for a single bond. (3 words)
- Stable structures formed by lipids in water, which are held together by hydrophobic interactions.
- $H_2PO_4^- \rightleftharpoons H^+ + PO_4^{2-}$ describes a _____ buffer system.
- Compound containing both polar and nonpolar regions.



- The electrostatic interactions between the hydrogen and oxygen atoms on adjacent H_2O molecules constitute a _____ (2 words)
- Dissolved molecules.
- Covalent bond breakage by the addition of water.
- Water molecules readily dissolve compounds such as NaCl because they screen _____ interactions between Na^+ and Cl^- .
- pH at which $[HAc] = [Ac^-]$.
- $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$ describes a _____ buffer system.
- Describes a solution in which $[H^+]$ is greater than $[OH^-]$.
- Noncovalent bonds have weaker bond _____ than covalent bonds.