# Lab 5B.    pH and Buffers—How can the pH of a Solution be Changed?

## Prelab Assignment

*Before* coming to lab:
- Read this lab handout thoroughly and then answer the ***pre-lab questions*** on page 15 of this lab exercise and hand them in at the start of your lab period.
- This lab exercise does *not* require a report in your lab notebook. The report for this exercise consists of completing the attached *Report Pages* (pp. 5 – 13) as you carry out the procedures on page 4.
- Prelab knowledge required: strong and weak acids and bases, pH, $K_a$, $pK_a$, buffers, pH of buffers, Henderson-Hasselbach equation

## Introduction: Buffers and the pH of Buffers

A **buffer** is a solution that resists changes in pH when small quantities of an acid or base are added to it. A **buffer** is made with a weak acid and a soluble salt containing the conjugate base of the weak acid <u>or</u> a weak base and a soluble salt containing the conjugate acid of the weak base. Some examples of buffer pairs are listed in table 1.

**Table 1.** Examples of buffers

| Weak Acid | Conjugate Base |
|---|---|
| acetic acid, $CH_3COOH$ | sodium acetate, $CH_3COONa$ |
| phosphoric acid, $H_3PO_4$ | potassium dihydrogen phosphate, $KH_2PO_4$ |
| sodium dihydrogen phosphate, $NaH_2PO_4$ | Sodium hydrogen phosphate, $Na_2HPO_4$ |
| carbonic acid, $H_2CO_3$ | sodium hydrogen carbonate, $NaHCO_3$ |
| ammonium Chloride, $NH_4Cl$ | Aqueous ammonia, $NH_{3(aq)}$ |

An **acidic buffer** solution has a pH less than seven. Acidic buffers are made from a weak acid with a $pK_a$ close to the desired pH and a conjugate base to go with it. An **alkaline buffer** solution has a pH greater than 7. Alkaline buffers are commonly made from a weak base (e.g. $NH_{3(aq)}$) and a salt of its conjugate acid (e.g. $NH_4Cl$)

**How do buffers resist changes in pH?** If we mix a weak acid (HA) with its conjugate base (A⁻), both the acid and base components remain present in the solution in relatively high concentration. This is because they do not undergo any reactions that significantly alter their concentrations. The acid and conjugate base may react with one another, $HA + A^- \rightarrow A^- + HA$, but when they do so, they simply trade places and the concentrations of HA and A⁻ do not change. Moreover, HA and A⁻ only rarely react with water since by definition, a weak acid is one that only *rarely* dissociates in water (that is, only rarely will the acid lose its proton H⁺ to water). Likewise, since the conjugate base A⁻ is a weak base, it *rarely* steals a proton H⁺ from water.

Hence, the concentration of weak acid, HA, and weak base, A-, remain in the solution with high concentrations since they only rarely react with the water. However, they are very likely to react with any added strong base or strong acid.

**How does a buffer neutralize a strong base?** When a strong base is added to a buffer, the weak acid, HA, gives up its $H^+$ to the added base ($OH^-$) to form water ($H_2O$) and the conjugate base of the weak acid:

$$HA + OH^- \rightarrow A^- + H_2O.$$
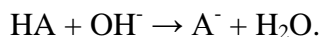
Since the added $OH^-$ is consumed by this reaction, the pH will change only slightly.

**How does a buffer neutralize a strong acid?** If a strong acid is added to a buffer, the weak base will react with the $H^+$ from the strong acid to form the weak acid HA:

$$H^+ + A^- \rightarrow HA.$$
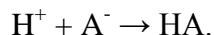
The $H^+$ gets absorbed by the $A^-$ instead of reacting with water to form $H_3O^+$ ($H^+$), so the pH changes only slightly.

**What determines the pH of a buffer?** The pH of a buffer is determined by two factors: 1.) The acid dissociation constant, $K_a$, of the weak acid and 2.) the ratio of weak base $[A^-]$ to weak acid $[HA]$ in the buffer solution.

1.) Each weak acid has its own acid dissociation constant, $K_a$. The $K_a$ tells us what proportion of HA will be dissociated into $H^+$ and $A^-$ in solution. The larger the $K_a$ value, the higher the concentration of $H^+$ ions present in solution, the more acidic and lower the pH of the resulting solution.

$$HA \rightleftharpoons H^+ + A^-$$

Eqn 1. $\quad K_a = \dfrac{[H^+][A^-]}{[HA]}$

2.) The ratio of $[A^-]$ to $[HA]$ in a buffer also affects the pH. If a buffer has more weak base than weak acid (i.e. $[A^-] > [HA]$), then more $OH^-$ ions are likely to be present and the pH will rise. If a buffer has more acid than base (i.e. $[HA] > [A^-]$), then more $H^+$ ions are likely to be present and the pH will fall. When the concentrations of $A^-$ and HA are equal, the concentration $H^+$ is equal to $K_a$, (or equivalently $pH = pK_a$).

**The Henderson-Hasselbach (H-H) Equation is used to calculate the pH of a Buffer.**

Derivation of the H-H Equation: Solving eqn. 1, above, for $[H^+]$ yields eqn. 2:

Eqn 2. $\quad [H^+] = \dfrac{K_a[HA]}{[A^-]}$

Which is the same as...

Eqn 3. $\quad [H^+] = (K_a)\left(\dfrac{1}{[A^-]}\right)([HA])$

The **Henderson-Hasselbach (H-H) equation** is the *negative log* of the equation 3. Below is the negative log of each component in equation 3:

$-\log[H^+] = pH \qquad -\log K_a = pK_a \qquad -\log(1/[A^-]) = +\log[A^-] \qquad -\log([HA]) = -\log[HA]$

Taking the negative log of equation 3 yields the Henderson-Hasselbach equation (equation 4)...

$$pH = pK_a + \log[A^-] - \log[HA], \text{ which is the same as...}$$

$$pH = pK_a - \log([HA]/[A^-]), \text{ which is the same as...}$$

Eqn. 4. $\quad \mathbf{pH = pK_a + \log([A^-]/[HA]),}$ the usual way you see the H-H equation.

**Table 2.** Four different ways to express the *Henderson-Hasselbach equation*.

$$pH = pK_A - \log \frac{[HA]}{[A^-]}$$

*or*

$$pH = pK_A + \log \frac{[A^-]}{[HA]}$$

*or*

$$pOH = pK_B + \log \frac{[\text{conjugate cation}]}{[\text{base}]}$$

*or*

$$pOH = pK_B - \log \frac{[\text{base}]}{[\text{conjugate cation}]}$$

An *equimolar buffer* is one in which the concentration of the weak acid (or base) is the same as the concentration of the conjugate ion. This may not seem particularly significant to you, but there are several important ideas that can be easily seen from it. Start with the ionization equilibrium expression and cancel the [HA] with the [A⁻]. This shows that for an *equimolar buffer $K_a = [H^+]$.*

$$k_A = \frac{[H^+][A^-]}{[HA]}$$

$$\text{if } [HA] = [A^-]$$

$$k_A = [H^+]$$

Now let's do a similar trick with the H-H equation. If [HA] = [A⁻], then the term [HA]/[A⁻] = 1 and log 1 = 0, so pH = pK**a**.

$$pH = pK_A - \log \frac{[HA]}{[A^-]}$$

$$pH = pK_A$$

This indicates that in an *equimolar buffer* the *pH = pKa* and that the RATIO of the [HA] to [A⁻] will determine the pH of the solution. The further the ratio gets from one to one, the further the pH gets from the pK**a**. *A buffer has its greatest buffering power at or near the pKa of the weak acid (or base)*. The higher the concentration of both the weak acid and its conjugate ion, the more buffering power is available.

(*Acknowledgement*: this introduction was adapted from similar pages found at www.chemtutor.com and http://www.chemcollective.org)

## Overview of the Procedure

Part 1. You will begin by calculating the pH of 50 mL of water to which HCl and NaOH have been added in increments. Then a pH meter or pH probe will be used to measure the pH of the solutions.

Part 2. The same experiment is repeated from Part 1, but 50 mL of a solution containing acetic acid and sodium acetate will be used in place of the water.

Part 3. This part involves a carbonate buffer ($HCO_3^-/CO_3^{2-}$) and introduces additional buffers ($H_2PO_4^-/HPO_4^{2-}$, $NH_4^+/NH_3$) in the skill development questions.

## Procedure

### Part 1: What's the pH?          (Work in teams of 2)

| **Special Equipment** | **Chemicals Required** |
| --- | --- |
| – 1 mL pipette | – 10 mL 0.20 HCl |
| – Pipette bulb | – 10 mL 0.20 NaOH |
| | – Boiled D.I. water |

<u>Addition of HCl to water</u>

a. Calculate the pH expected when 5.0 mL of 0.20 M HCl is added to 50.0 mL of D.I. water in 1.0 mL increments. Record your answers in table 1.

b. Set up the pH recording apparatus and record the pH of *freshly boiled* D.I. water.

c. Carry out the experiment described in step a, above, by adding 0.20 M HCl to 50.0 mL *freshly boiled D.I. water*. Add the HCl solution in 1.0 mL increments up to a total addition of 5.0 mL and record the total volume and pH after each addition of HCl in table 1.

<u>Addition of NaOH to water</u>

d. Calculate the pH expected when 5.0 mL of 0.20 M NaOH is added to 50.0 mL of D.I. water in 1.0 mL increments. Record your answers in table 2.

e. Setup the pH recording apparatus and record the pH of freshly boiled distilled water.

f. Carry out the experiment described in step d, above, by adding 0.20 M NaOH to 50.0 mL *freshly boiled D.I. water*. Add the NaOH solution in 1.0 mL increments up to a total addition of 5.0 mL and record the total volume and pH after each addition of NaOH in table 2.

### Part 2. What's the pH Revisited          (Work in teams of 2)

| **Special Equipment** | **Chemicals Required** |
| --- | --- |
| – 1 mL pipette | – 100 mL solution consisting of 0.50 M acetic acid and 0.50 M sodium acetate |
| – Pipette bulb | – 10 mL 0.20 HCl |
| | – 10 mL 0.20 NaOH |

a. Obtain 50.0 mL of a solution that consists of the 0.50 M acetic acid and 0.50 M sodium acetate. Record the pH of 50.0 mL of this solution in table 3.

b. Repeat the addition of HCl described in Part 1 to 50.0 mL of the solution consisting of 0.50 acetic acid and 0.50 M sodium acetate. Record the volume and the pH after each addition in table 3.

c. Repeat the addition of NaOH described in part 1 to 50.0 mL of a *fresh* solution consisting of 0.50 M acetic acid and 0.50 M sodium acetate. Record the volume and the pH after each addition in table 4.

### Part 3.  What's the Solution?          (Work in teams of 2)

| **Special Equipment** | **Chemicals Required** |
| --- | --- |
| – 100 mL volumetric flask | – Sodium carbonate powder |
| | – Sodium hydrogen carbonate powder |

a. You have available solid sodium carbonate, $Na_2CO_3$, sodium hydrogen carbonate, $NaHCO_3$, and DI water. How could you prepare 100.0 mL of a solution that will maintain a pH of 10.3? The $K_a$ of the hydrogen carbonate ion, $HCO_3^{1-}$, is 4.7 x $10^{-11}$. Show your work in table 5.

b. Prepare 100.0 mL of the solution and then measure its pH with the pH probe. Record the pH in table 5.

**Lab 5B Report Sheet**

**pH and Buffers**

Name _____

Team No. _____Date _____Section _____

## *Experimental Results*

### Part 1 Data and Observations

**Table 1.** Addition of 0.20 M HCl to DI Water

| Volume 0.20 M HCl added to 50.0 mL boiled DI $H_2O$ (mL) | Calculated pH | Measured pH | Sample Calculation |
|---|---|---|---|
| 0.0 | | | |
| 1.0 | | | |
| 2.0 | | | |
| 3.0 | | | |
| 4.0 | | | |
| 5.0 | | | |

**Table 2.** Addition of 0.20 M NaOH to DI Water

| Volume 0.20 M NaOH added to 50.0 mL boiled DI $H_2O$ (mL) | Calculated pH | Measured pH | Sample Calculation |
|---|---|---|---|
| 0.0 | | | |
| 1.0 | | | |
| 2.0 | | | |
| 3.0 | | | |
| 4.0 | | | |
| 5.0 | | | |

**Part 2 Data and Observations**

**Table 3.** Addition of 0.20 M HCl to 50.0 mL 0.50 M acetic acid - 0.50 M sodium acetate solution

| Volume 0.20 M HCl added to 50.0 mL 0.50 M acetic acid – 0.50 M sodium acetate (mL) | Calculated pH | Measured pH |
|---|---|---|
| 0.0 | | |
| 1.0 | | |
| 2.0 | | |
| 3.0 | | |
| 4.0 | | |
| 5.0 | | |

**Table 4.** Addition of 0.20 M NaOH to 50.0 mL 0.50 M acetic acid - 0.50 M sodium acetate solution

| Volume 0.20 M NaOH added to 50.0 mL 0.50 M acetic acid – 0.50 M sodium acetate (mL) | Calculated pH | Measured pH |
|---|---|---|
| 0.0 | | |
| 1.0 | | |
| 2.0 | | |
| 3.0 | | |
| 4.0 | | |
| 5.0 | | |

**Part 3 Data and Observations**

**Table 5.** Carbonate - Bicarbonate buffer

| Masses added to 100 mL volumetric flask (g) | | Desired pH | Measured pH |
|---|---|---|---|
| **$Na_2CO_3$** | **$NaHCO_3$** | 10.3 | |
| Calculation of mass of $Na_2CO_3$ and $NaHCO_3$ required: | | | |

## *Analysis of the Results*

**Critical Thinking Questions for Part 1**

1. Write a balanced chemical equation that describes the reaction when HCl is added to water. What is the approximate $K_a$ for this reaction? <u>Explain</u>.

2. Do your calculations of the pH agree with the experiment? What happens to the pH when acid is added to water? <u>Explain any discrepancies between the calculated and measured pH values</u>.

3.  Write a balanced chemical equation that describes the reaction when solid NaOH is added to water. What is the approximate $K_b$ for this reaction? Explain.

4.  Do your calculations of the pH agree with the experiment? What happens to the pH when base is added to water?  Explain any discrepancies between the calculated and measured pH values.

**Critical Thinking Questions for Part 2**

1.  Compare the change in pH produced after the addition of each one mL increment of acid (HCl) to pure water and the acetic acid-sodium acetate solution used in part 2. What conclusions can you reach?

2.  Compare the change in pH produced after the addition of each one mL increment of base (NaOH) to pure water and the acetic acid-sodium acetate solution part 2. What conclusions can you reach?

3.  Write an equation that describes the reaction of acetic acid, $CH_3COOH$, with water.

4.  a.)  Why is $CH_3COOH$ an acid?

    b.) What is the formula of the conjugate base of $CH_3COOH$? _____

5.  Write an equation that describes the reaction of sodium acetate, $CH_3COONa$, with water.

6.  a.)  Is $CH_3COONa$ an acid or a base? *Explain*.

    b.) What is the formula of the conjugate acid of $CH_3COONa$? _____

7.  Write a balanced chemical equation that describes what happens when NaOH solution is added to an acetic acid solution.

8.  Explain the observations made when NaOH solution is added to the acetic acid–sodium acetate solution.

9.  Write a balanced chemical equation that describes what happens when HCl is added to a sodium acetate solution.

10. Explain the observations made when HCl solution is added to the acetic acid–sodium acetate solution.

**Part 2. Skill Development Questions**

1. The $K_a$ of acetic acid is 1.75 x $10^{-5}$. Calculate the pH of the following solutions. *Show your work*.

   a.) A solution consisting of 0.50 M acetic acid and 0.50 M sodium acetate. *Circle your answer*.

   b.) A solution consisting of 0.10 M acetic acid and 0.50 M sodium acetate. *Circle your answer*.

2. Suppose it is desired to maintain the pH of a solution at 4.2 using only acetic acid and sodium acetate, describe how this could be done. *Show your work* and *circle your answer.*

3. How would you prepare a solution of acetic acid and sodium acetate that maintains a pH of 5.2? Show your work. *Show your work* and *circle your answer.*

4. Use the computer simulation "pH of Buffers" found at the Lab section of the Chem 163 class website to test your responses to skill development questions 1-3, above. Use equal volumes of acetic acid and sodium acetate and remember to consider the effect of dilution on their concentrations upon mixing.

5. Use *Excel* to make a graph of the pH of the solutions from skill development questions 1-4, above, against an appropriate quantity to produce a straight line with a positive slope. Cut and past the graph into the space below.  Hint: the H-H equation, $pH = pK_a + \log([A^-]/[HA]$, is  in the form of the equation of a line, $y = b + mx$.

**Skill Development Questions for Part 3**

1. Using only sodium carbonate, sodium hydrogen carbonate and DI water, how could you prepare solutions of pH = 9.9 and pH = 10.5? *Show your work* and *circle your answer.*

2.  What would be the pH of a solution of 0.50 M $NaH_2PO_4$ and 0.50 M $Na_2HPO_4$? The $K_a$ for $H_2PO_4^-$ is 6.3 x $10^{-8}$ and the $K_a$ for the $HPO_4^{2-}$ is 4.2 x $10^{-13}$. *Show your work* and *circle your answer.*

3.  What is the pH of a solution of 0.50 M $NH_3$ and 0.50 M $NH_4Cl$? The $K_a$ for $NH_4^+$ is 5.6 x $10^{-10}$ and the $K_b$ for $NH_3$ is 1.8 x $10^{-5}$. *Show your work* and *circle your answer.*

4.  Consider the four buffers studied in parts 2 and 3 above ($CH_3COOH/CH_3COO^-$, $HCO_3^-/CO_3^{2-}$, $H_2PO_4^-/HPO_4^{2-}$ and $NH_4^+/NH_3$) when answering the following questions. *Hint*: consider the $pK_a$ of the weak acid in these buffers when answering questions a and b, below.
    a.) Describe two ways to prepare a solution that will maintain pH = 6. *Show your work* and *circle your answer.*
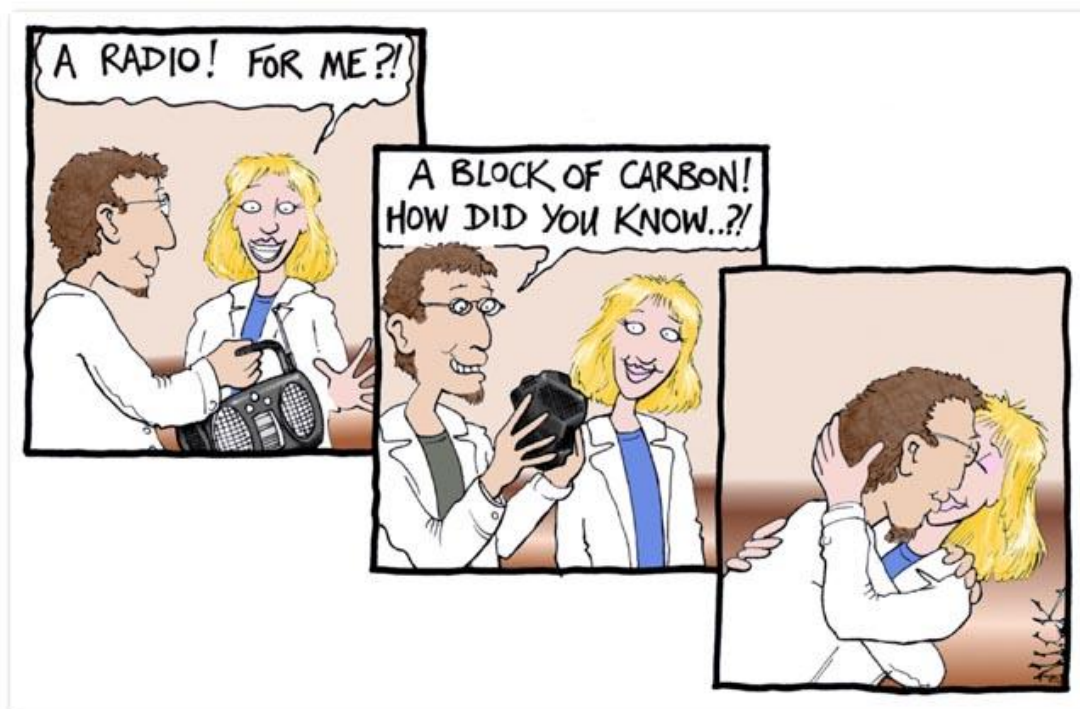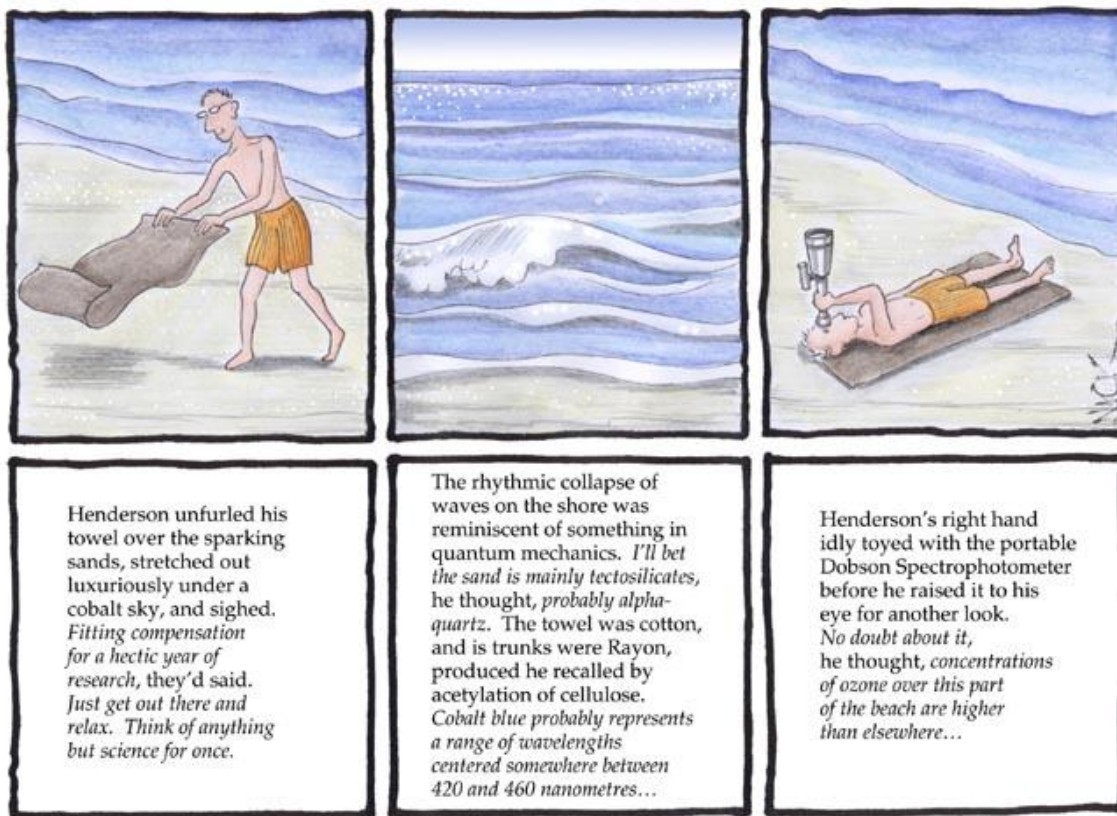
b.) Describe two ways to use different combinations of acid and conjugate base to obtain a pH = 9.5. *Show your work* and *circle your answer.*

c.) Will the pH of any of these buffer solutions change if the solution is diluted? *Explain*.

5. In general, how would you tell someone to prepare a solution that resists change in pH?

## *Therapeutic Buffer Space and Cartoons Provided at No Extra Cost...*



Henderson unfurled his towel over the sparking sands, stretched out luxuriously under a cobalt sky, and sighed. *Fitting compensation for a hectic year of research*, they'd said. *Just get out there and relax. Think of anything but science for once.*

The rhythmic collapse of waves on the shore was reminiscent of something in quantum mechanics. *I'll bet the sand is mainly tectosilicates*, he thought, *probably alpha-quartz.* The towel was cotton, and is trunks were Rayon, produced he recalled by acetylation of cellulose. *Cobalt blue probably represents a range of wavelengths centered somewhere between 420 and 460 nanometres...*

Henderson's right hand idly toyed with the portable Dobson Spectrophotometer before he raised it to his eye for another look. *No doubt about it,* he thought, *concentrations of ozone over this part of the beach are higher than elsewhere...*



The radiocarbon dating technique.

*Lab 5B. Prelab Questions*
*pH and Buffers*

**Name** _____

**Date** _____**Section** _____**Group No.**_____

**Instructions**: Complete the following questions and hand in at the start of your lab period. Clearly and neatly show your work with units and correct significant figures for all questions that involve a calculation.

Calculate the pH of the following solutions. *Circle your answers.*

1. A solution produced by adding 4.0 mL 0.10 M $HNO_3$ to 30.0 mL DI water

2. A solution produced by adding 4.0 mL 0.10 M KOH to 30.0 mL DI water

The $K_a$ of lactic acid, $CH_3CH(OH)COOH$, is 8.32 x $10^{-4}$. Calculate the pH of the following solutions. *Circle your answers.*

3. A solution consisting of 0.25 M lactic acid and 0.25 M sodium lactate

4. A solution consisting of 0.15 M pro lactic acid and 0.25 M sodium lactate