

Report: Buffer Solutions

Name: ANSWER KEY Bench #

Section: Date:

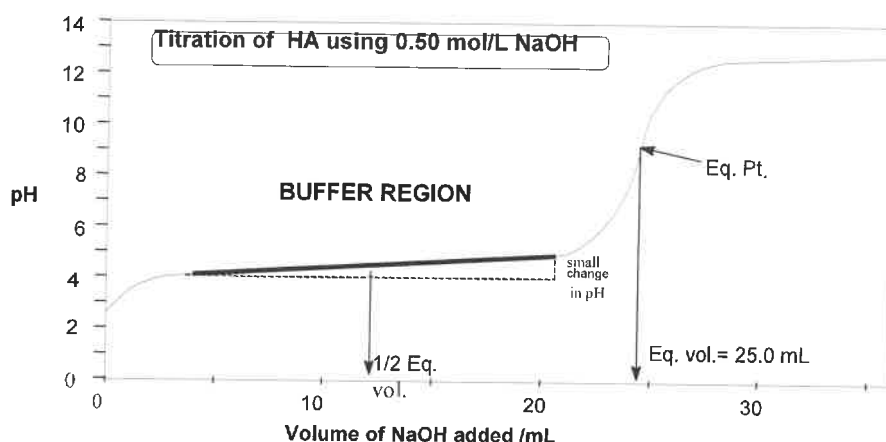
Laboratory Instructor:

Assessment

Preparation	<u> </u> /1
Quiz	<u> </u> /9
Deductions	<u> </u>
Total	<u> </u> /10

Dihydrogen phosphate-hydrogen phosphate buffer solutions

1. Draw a schematic plot of a pH titration curve and identify the buffer region and *the point* with the highest acid buffering capacity. Explain the function of a buffer and the reason for selecting the above point. (1.2)



Buffers are solutions in which a weak acid and its conjugate base are both present in concentrations that are high compared with the concentrations of H_3O^+ or OH^- .

These species present at equilibrium allow for the reaction of small amounts of added H_3O^+ or OH^- through shifts in the weak acid equilibrium. These shifts consume most of the added H_3O^+ or OH^- and maintain a relatively constant $[\text{H}_3\text{O}^+]$ and pH.

The point of highest buffer capacity is at $\frac{1}{2}$ the equivalence volume since the concentrations of acetic acid and acetate ion are equal at this point. The maximum amounts of either H_3O^+ or OH^- added can be reacted.

2. Compare the pH of the original buffer solution and the 1/5 diluted buffer solution. Using the K_a relation or the Henderson-Hasselbach equation, explain why the change in pH was so small compared to the change in concentrations. (0.7)

$$\text{pH} = \text{p}K_a + \log (\text{base/acid})$$

The pH is about the same for both solutions.

The ratio of the concentrations of A^- and HA will remain the same in the diluted buffer as in the original solution since both are being changed by the same dilution factor $\therefore$ the log factor is constant so the pH will remain $\sim$ constant.

There are limits. When “x” becomes significant, the Henderson-Hasselbach equation can no longer be used. The 10 fold dilution done here does not exceed these limits.

3. a) What was the change in pH when 2 drops of HCl was added to the water?

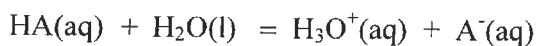
decrease of 3 to 5 pH units

- b) Fill in the following Table.

Buffer	Initial pH	pH change	volume HCl required /mL	volume NaOH required /mL
buffer	≈ 4.75	first pH unit	10–12	10–12
buffer		second pH unit	1–2	1–2
dilute buffer	≈ 4.75	first pH unit	1–2	1–2
dilute buffer		second pH unit	drops	drops
commercial buffer	≈ 7.00	first pH unit	2–3	2–3
commercial buffer		second pH unit	≈ 0.5	≈ 0.5

- c) Use the weak acid dissociation equilibrium and LeChâtelier's Principle to explain the effect of adding H^+ (in the form of the strong acid HCl) to the buffer solution.

i) For the 1st pH unit change. (0.4)



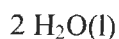
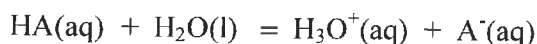
If a small amount of H_3O^+ is added to a buffer solution, the position of the weak acid equilibrium will shift to the left, reacting the added H_3O^+ with A^- to form more HA which consumes most of the added H_3O^+ . Therefore, there is no dramatic change in $[\text{H}_3\text{O}^+]$ and the pH remains relatively constant.

ii) For the 2nd pH unit change. (0.4)

Much less HCl is required for the 2nd pH unit change because most of the A^- (conjugate base) has been reacted by the H_3O^+ addition for the 1st change. Once all the A^- has been completely reacted through the addition of H_3O^+ , there is nothing left in solution to react (consume) with the added H_3O^+ . Therefore, H_3O^+ will remain free in solution and the pH will decrease dramatically, i.e. the capacity of the buffer has been exceeded.

- d) Use the weak acid dissociation equilibrium and LeChâtelier's Principle to explain the effect of adding OH^- (in the form of the strong base NaOH) to the buffer solution.

i) For the 1st pH unit change. (0.4)

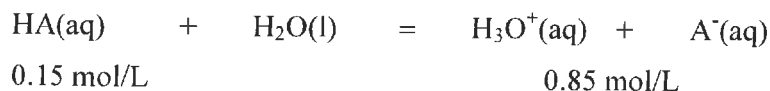
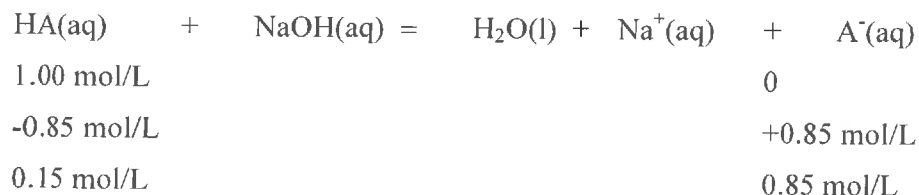


If a small amount of OH^- is added to a buffer solution, it will react with H_3O^+ . The $[\text{H}_3\text{O}^+]$ will decrease and the position of weak acid equilibrium will shift to the right causing more HA to dissociate to replace the depleted H_3O^+ . Again there is no dramatic change in the $[\text{H}_3\text{O}^+]$ occurs, maintaining a relatively constant pH.

ii) For the 2nd pH unit change. (0.4)

Much less NaOH is required for the 2nd pH unit change because most of the HA (weak acid) has been reacted by the OH^- addition for the 1st change. Once all the HA has been completely reacted through the addition of OH^- , there is nothing left in solution to replace the depleted H_3O^+ . Therefore, the OH^- added will remain free in solution and the pH will increase dramatically, i.e. the capacity of the buffer has been exceeded.

3. A 1.00 mol/L solution of an unknown monoprotic acid is titrated with NaOH. When 85.0 % of this weak acid has reacted, the pH of the resulting solution at equilibrium is 5.33. Determine the K_a for this weak acid. (1.0)



This is a buffer (mixture of HA and A^-): OR $[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-5.33} = 4.68 \times 10^{-6} \text{ mol/L}$.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$5.33 = \text{p}K_a + \log \left(\frac{0.85 \text{ mol/L}}{0.15 \text{ mol/L}} \right)$$

$$5.33 - 0.753 = \text{p}K_a = 4.577$$

$$K_a = 10^{-4.577} = 2.7 \times 10^{-5}$$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA(aq)}]}$$

$$K_a = \frac{(4.68 \times 10^{-6})(0.85)}{(0.15)}$$

$$K_a = 2.7 \times 10^{-5}$$

4. You wish to buffer a solution at pH 1.26. If equal amounts of the acid and conjugate base are used, what is the best choice for the acid – conjugate base pair? (Use only the acids on your data sheet).

The best buffering capacity is when the acid in the buffer pair has a value of $\text{p}K_a$ equal to the pH.

$$\text{p}K_a = 1.26 \quad K_a = 10^{-1.26} = 5.50 \times 10^{-2}$$

The acid with the closest K_a value is dichloroacetic acid ($K_a = 5.48 \times 10^{-2}$).

The best buffer pair is $\text{CHCl}_2\text{COOH} / \text{CHCl}_2\text{COONa}$.

4. Calculate the volume of 0.25 mol/L sodium dihydrogen phosphate that must be added to 150 mL of 0.50 mol/L sodium hydrogen phosphate to prepare a buffer solution of pH 7.400. (1.5)

$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$$5.00 = -\log(1.76 \times 10^{-5}) + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$5.00 = 4.754 + \log \frac{\left(\frac{\text{mol CH}_3\text{COO}^-}{0.150 \text{ L} + V_{\text{CH}_3\text{COOH}}} \right)}{\left(\frac{\text{mol CH}_3\text{COOH}}{0.150 \text{ L} + V_{\text{CH}_3\text{COOH}}} \right)} \quad \text{Volume in denominator cancels}$$

$$0.24_6 = \log \left(\frac{\text{mol CH}_3\text{COO}^-}{\text{mol CH}_3\text{COOH}} \right)$$

$$1.7_6 = \left(\frac{\text{mol CH}_3\text{COO}^-}{\text{mol CH}_3\text{COOH}} \right) = \left(\frac{[\text{CH}_3\text{COO}^-] \cdot V_{\text{CH}_3\text{COO}^-}}{[\text{CH}_3\text{COOH}] \cdot V_{\text{CH}_3\text{COOH}}} \right) = \left(\frac{0.50 \text{ mol/L} \times 0.150 \text{ L}}{0.25 \text{ mol/L} \times V_{\text{CH}_3\text{COOH}}} \right)$$

$$V_{\text{CH}_3\text{COOH}} = 0.17 \text{ L}$$

Capacity of the buffer solutions

1. a) Determine the acid and base buffer capacities of each HA and A⁻ (in mol L⁻¹) of:
i) the buffer solution. (0.3)

Acid capacity of buffer =

$$\frac{\text{moles acid needed to decrease pH by 1 unit}}{\text{volume of buffer used}} = \frac{(0.10 \text{ mol/L})(\sim 0.02000 \text{ L})}{0.0200 \text{ L}} = 0.10 \text{ mol/L}$$

Base capacity of buffer =

$$\frac{\text{moles base needed to increase pH by 1 unit}}{\text{volume of buffer used}} = \frac{(0.10 \text{ mol/L})(\sim 0.02000 \text{ L})}{0.0200 \text{ L}} = 0.10 \text{ mol/L}$$

- ii) the dilute buffer solution (0.3)

Acid capacity of buffer =

$$\frac{\text{moles acid needed to decrease pH by 1 unit}}{\text{volume of buffer used}} = \frac{(0.10 \text{ mol/L})(\sim 0.00200 \text{ L})}{0.0200 \text{ L}} = 0.010 \text{ mol/L}$$

Base capacity of buffer =

$$\frac{\text{moles base needed to increase pH by 1 unit}}{\text{volume of buffer used}} = \frac{(0.10 \text{ mol/L})(\sim 0.00200 \text{ L})}{0.0200 \text{ L}} = 0.010 \text{ mol/L}$$

ii) the commercial pH 7.00 buffer solution. (0.3)

Acid capacity of buffer =

$$\frac{\text{moles acid needed to decrease pH by 1 unit}}{\text{volume of buffer used}} = \frac{(0.20 \text{ mol/L})(\sim 0.0020 \text{ L})}{0.0200 \text{ L}} = 0.020 \text{ mol/L}$$

Base capacity of buffer =

$$\frac{\text{moles base needed to increase pH by 1 unit}}{\text{volume of buffer used}} = \frac{(0.20 \text{ mol/L})(\sim 0.002 \text{ L})}{0.0200 \text{ L}} = 0.020 \text{ mol/L}$$

- b) Use the above information to explain why it is important that the pH electrode be washed well with deionized water before it is placed into the standard buffer solutions. (Assume that each bottle of buffer solution contains 50 mL of commercial buffer.) (0.6)

In 50 mL of standard buffer solution, the moles of base needed to increase or decrease the pH unit will be very small.

Using the buffer capacity calculated above, moles base or acid needed to change pH by 1 unit = $(0.020 \text{ mol/L})(0.050 \text{ L}) = 0.0010 \text{ mol}$.

The volume of 0.20 mol/L NaOH or HCl required to change the pH by 1 unit = $(0.0010 \text{ mol}) / (0.20 \text{ mol/L}) = 0.00020 \text{ L} = 0.2 \text{ mL}$ (less than 1 drop)

If the electrode is not rinsed before placing it in the standard buffers, the pH of the standard buffers will change and the pH meter will not be calibrated properly.

2. Comment on the differences in buffering capacity of the original buffer and the diluted buffer. Should they be nearly the same or very different? Explain. (1.5)

The buffer capacity is less for the diluted buffer. There are two reasons for this.

First, the buffer was diluted and a larger volume was used, thereby decreasing the buffer capacity (according to the definition above).

Second, only half of the diluted volume was used. Half of the moles of HA and A⁻ were present in each set of 100 mL and this also decreased the buffer capacity by decreasing the volume of acid or base needed to change the pH by 1 unit.

P-16 Q6

$$7.400 = -\log(6.29 \times 10^{-8}) + \log\left(\frac{n_{A^-}}{n_{HA}}\right) \quad \begin{array}{l} A^- = \text{HPO}_4^{2-} \\ HA = \text{H}_2\text{PO}_4^- \end{array}$$

$$7.400 = 7.201 + \log\left(\frac{n_{A^-}}{n_{HA}}\right)$$

$$0.200 = \log\left(\frac{n_{A^-}}{n_{HA}}\right)$$

$$1.58 = \frac{n_{A^-}}{n_{HA}} = \frac{0.150 \times 0.50}{0.25 \times V_{HA}}$$

$$0.25 \times V_{HA} = 0.0475 \quad V = 0.189 \text{ L}$$