LAB 6: Buffer solutions

Introduction

Buffers or buffer solutions are systems of a mixture of compounds in aqueous solutions, which possess the property of resisting changes in pH upon the addition of small amounts of a strong acid or base.

Buffers are of 2 types:

a. ***Acidic buffer***: it is a combination of a weak acid and its salt (its conjugate base), an example is acetic acid and sodium acetate buffer solution.
b. ***Basic buffer***: it is a combination of a weak base and its salt (its conjugate acid), an example is ammonium hydroxide and ammonium chloride buffer solution.

Note: the salt of an acid is treated as a base and vice versa, for example:

Acetic acid (weak acid), has a salt, sodium acetate which is considered as a base.
Ammonia is a base, but its salt, ammonium chloride is considered as an acid.

Q: How does a buffer system resist the change in pH?

A: Let's take acetic acid/sodium acetate buffer system to which NaOH (strong base) is added as an example:

$$CH_3COOH + H_2O \longleftrightarrow H_3O^+ + CH_3COO^-$$

$$CH_3COONa \longrightarrow Na^+ + CH_3COO^-$$

If a strong acid (H_3O^+) is added (e.g., HCl), the acetate ion provided mainly by the salt, ties up the hydrogen ions removing them from solution as undissociated weak acid according to the reaction:

$$CH_3COO^- + H_3O^+ \longleftrightarrow CH_3COOH + H_2O$$

If a strong base is added (e.g., NaOH), acetic acid neutralizes the hydroxyl ion to form undissociated water as follows:

$$CH_3COOH + OH^- \longleftrightarrow CH_3COO^- + H_2O$$

In case of basic buffer, the buffering action of a mixture of a weak base and its salt arises from the removal of H^+ ions by the base to form the salt and removal of OH^- ions by the salt to form undissociated water.

Factors influencing the pH of a buffer solution:

1. **Addition of neutral salts** to buffers changes the pH of the solution by altering the ionic strength.
2. **Dilution** also changes the ionic strength of a buffer system and hence the pH of such a system may be affected. The addition of water in moderate amounts will not markedly change the pH but it may cause a small positive or negative deviation because it alters the activity coefficients and because water itself can act as a weak acid or base.
3. **Temperature**: the pH of acetate buffer was found to increase with temperature whereas the pH of boric acid-sodium borate system decreases with temperature.

The buffer equations (Henderson Hasselbalch equations):

The buffer equation is useful for:

a. calculating the pH of a buffer system of known composition
a. calculating the concentration of buffer components required to maintain a solution at the required pH
b. calculating the change in pH of a buffered solution upon the addition of a given amount of an acid or base.

The buffer equation is satisfactory for calculations within pH range from 4 to 10.

For weak acid and its salt	$pH = pK_a + \log\frac{[ionized]}{[un\text{-}ionized]}$	$pH = pK_a + \log\frac{[salt]}{[acid]}$
For weak base and its salt	$pH = pK_a + \log\frac{[un\text{-}ionized]}{[ionized]}$	$pH = pK_w - pK_b + \log\frac{[base]}{[salt]}$ Or $pH = pK_a + \log\frac{[base]}{[salt]}$

Buffer Capacity (β)

is a function that measures the ability of a buffer to resist changes in pH.
Buffer capacity can be defined as being equal to the amount of strong acid or strong base, expressed as moles of H^+ or OH^- ion, required to change the pH of 1 litre of the buffer by one pH unit.
(in other words: it is expressed as the molarity of sodium hydroxide required to increase pH by 1.0)

Buffer capacity can be measured in millimoles of acid (or base) per liter of buffer, using Van Slyke equation:

$$\beta = \frac{\Delta B}{\Delta pH}$$

Where ΔpH is the change in pH, while ΔB is the small increment of strong base in millimoles (gm equivalent/liter).

Buffer capacity is not a fixed value, it is affected by:

- Concentration of buffer components: it increases as the concentrations of the buffer components increase.
- Ratio of the concentrations of weak acid and its salt, maximum capacity being obtained when the ratio of acid to salt = 1 (i.e., the buffer capacity is maximum when pH = pKa)
- Amount of base (acid) added

Example:

0.5 ml of 0.1 M NaOH is added to 40 ml of buffer solution having pH 3.75. The pH changed to 3.78. Calculate the buffer capacity.

Answer:

$$\beta = \frac{\Delta B}{\Delta pH}$$

Δ pH =3.78 – 3.75 = 0.03

0.1 M NaOH =0.1 N NaOH (because the Eq. wt = M.wt)

Since the volume of solution changed, we must calculate the concentration in the new volume as follows:

$C_1 V_1 = C_2 V_2$

$0.1 \times 0.5 = C_2 \times (40+0.5)$ ml

C_2=0.0012 N is the normality of NaOH in the final solution

Thus: buffer capacity will be:

$\beta = 0.0012 / 0.03$

$= 0.04$ N

Methods of pH measurement

1. **Mathematical method**: by using the *Handerson-Hasselbalch equation*
2. **Colorimetric methods (approximate methods)**:

This is a simple and inexpensive method for determining the approximate pH of a solution. It is less accurate than the electrometric method, but can be used in the determination of the pH of aqueous solutions which are not colored or turbid.
Determination of pH by colorimetric methods involves the use of:

a. ***Paper indicators****:* A strip of paper that undergo color changes depending on the pH of the solution where the strip is immersed.

A drop of the solution is placed on a piece of the indicator paper and the resulting color is compared to a color chart supplied with the indicator paper. These papers are available in a wide variety of pH ranges.

- Basic litmus paper is blue in color; it turns red under acidic conditions,
- Acidic litmus paper is red in color; turns blue under basic (i.e. alkaline) conditions.
- Neutral litmus paper is also available, it is purple in color.

b. ***Liquid indicators****:*

pH can be measured by addition of a pH indicator into the solution under study.
Indicators are weak organic acids or bases whose degree of dissociation varies with the pH of the solution. Thus, the color of an indicator is a function of the pH of the solution; in acidic solution the indicator will have a certain color and in basic solution it will have another color
An example is *universal liquid indicator*. It consists of a mixture of several indicators (e.g., methyl yellow, methyl red, bromothymol blue, thymol blue, and phenolphthalein which covers pH range 1-12).

Color	pH	Color	pH
Red	1	Greenish yellow	7
Pink	2	Green	8
Orange-pink	3	Greenish blue	9
Orange	4	Blue	10
Orange-yellow	5	Violet	11
Yellow	6	Purple	12

3. Electrometric method (accurate method: by using pH meter):

A pH meter is an electronic instrument used to measure the pH of a liquid.

A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading.

In addition to the pH probe, there is a temperature probe in most types of pH meters.

The pH probe measures pH as the activity of hydrogen ions surrounding a thin-walled glass bulb at its tip. The probe produces a small voltage (about 0.06 volt per pH unit) that is measured and displayed as pH units by the meter.

The method of measurement by pH meter is as follows:

1. Turn on the power and plug the device on
2. Adjust the temperature knob at room temperature
3. Standardize the pH meter as follows:
   Remove the electrode from its storage cap. Rinse it with D.W from a washing bottle into an empty beaker. Blot the electrode (do not rub) on a filter paper. Place the electrode in a standardization buffer solution. The recommended pH of calibration is in the region of measured pH of the solution as follows:
   - less than pH 7: pH 4.0 and pH 7.0
   - more than pH 7: pH 7.0 and pH 10.0

   Do not touch the bottom or sides of the beaker, and calibrate it so as to match the pH of the standard buffer solution. Wait for approx. 20 to 30 seconds (for display to show stable value), then use adjustment knob set value to 7.00. Repeat calibration using a second calibration solution as required.
4. Measure the pH of the solution as follows:
   After removing the electrode from the standardization solution, rinse it with DW and blot it, then insert it in the solution whose pH is to be measured. Allow the electrode sufficient time to reach equilibrium and observe the displayed pH.
5. Remove the electrode of pH meter, rinse it and blot it then sore it in its cap (contains 3 M KCl solution) if no further readings are required, or in a beaker containing DW if there are other measurement were to be made later by the device. Turn off the power.

   Note: In pH meters provided with a temperature control unit, it is advisable to determine temperature of buffer solution and set accordingly

Experimental work:

Objectives:

- Preparation of 100 mL of 0.2 M acetate buffer solution (composed of acetic acid and sodium acetate).
- Measurement of its pH by different method and comparing the results

Materials and Chemicals:

For the class:

3 central burettes the contents of which will be:

- **0.2 M Acetic acid solution (solution A):** 1 L is prepared by using 12 gm HAC (= 12 ml) which is placed in 1L volumetric flask, and the volume completed up to the mark)
- **0.2 M sodium acetate solution (solution B):** 1 L is prepared by using 16.4 gm sodium acetate which is placed in 1L volumetric flask, and the volume completed up to the mark)
- **100 ml of 0.1 N sodium hydroxide solution:** this is prepared by using 0.4 gm sodium hydroxide which is placed in 100 mL volumetric flask, and the volume completed up to the mark)

liquid universal indicator, paper indicator, pH meter, filter paper +empty 500 ml beaker + washing bottle near the pH meter

For each group: 50- or 100-ml conical flask, 50 ml volumetric flasks, 10 ml graduated pipette + pipette rubber bulb

Procedure:

1. **Buffer Preparation:**
   Each group will prepare 50 ml acetate buffer solutions with various ratios of acetic acid/sodium acetate as shown in the table below.

Group no.	Solution A (0.2 M acetic acid solution) (ml)	Solution B (0.2 M sodium acetate solution) (ml)	DW Up to
1	25	1.25	50 ml
2	23.15	1.8	50 ml
3	15.25	9.75	50 ml
4	10	15	50 ml
5	7.5	17.5	50 ml
6	5	19	50 ml
7	2.5	22.5	50 ml
8	1.4	25	50 ml

2. **pH measurement and Buffer capacity calculation:** the pH of each buffer solution is measured by using each of the following methods:

   a. ***Handerson-Hasselbalch equation***: use the equation to predict the pH of the buffer solution (compare this theoretical value with values obtained from experimental measurements). pKa for acetic acid is 4.76

   b. ***Colorimetric method:***

   - ***Paper indicator:*** immerse a strip of wide range pH paper into small quantity of buffer solution and observe the color changes of the paper.
   - ***Liquid universal indicator:*** add 2 drops of universal indicators to 10 ml buffer solution (to obtain 10 ml solution, transfer the prepared solution to a conical flask, then, withdraw 10 ml of it and re-transfer it to the volumetric flask. To this add the indicator). Compare the color result with color found on the bottle of liquid universal indicator.

   c. ***Electrometric method** (by using pH meter):*

   Put the electrode of the pH meter in the remaining 40 ml of buffer solution and read the pH (record it as pH_1), then add 1 ml of 0.1 N NaOH solution and remeasure its pH (record it as pH_2).

   Repeat this step using 40 ml DW: record pH_1 and pH_2 after adding 1 ml of 0.1 N NaOH solution. Calculate the buffer capacity for water and buffer and compare the results.

Example:

If 1 ml of 0.1 N NaOH solution is added to 40 mL of 0.2 M buffer solution having pH 3.75, the final pH will be 3.78. What is the buffer capacity?

Answer:

$$\beta = \frac{\Delta B}{\Delta pH}$$

$$\Delta pH = 3.78 - 3.75 = 0.03$$

$$C1V1 = C2V2$$

$$0.1 \times 1 = C_2 \times (40 + 1)$$

$$C_2 = 0.002$$

$$\beta = \frac{0.002 - 0}{0.03} = 0.066$$

3. Results and discussion:

Group no.	Color observed after addition of universal inidcator	pH (Colorimetric method)	pH_1 (by pH meter)	pH_2 (by pH meter after adding NaOH)	Buffer capacity
1					
2					
3					
4					
5					
6					
7					
8					