Al-Mustaqbal University
Department of Techniques of Fuel and Energy Engineering
First stage
Subject: analytical chemistry
Lecturer: Zahraa Salah Hadi
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Buffer Solution

A buffer is a solution that can resist pH change upon the addition of an acidic or basic components. It is able to neutralize small amounts of added acid or base, thus maintaining the pH of the solution relatively stable. This is important for processes and/or reactions which require specific and stable pH ranges.

In nature, there are many systems that use buffering for pH regulation. For example, the bicarbonate buffering system is used to regulate the pH of blood.

Types:

1- Acidic Buffer (pH < 7) weak acid + its sodium or potassium salt ethanoic acid sodium ethanoate
2- Alkaline Buffer (pH > 7) weak base + its chloride Ammonia ammonium chloride

Email: Zahraa.Salah.Hadi@uomus.edu.iq

1- Acidic buffer solutions

an acidic buffer solution is one which has a pH less than 7, and commonly made from a weak acid and one of its salts often a sodium salt. A common example would be a mixture of ethanoic acid and sodium ethanoate in solution.

In this case, if the solution contained equal molar concentrations of both the acid and it salt, it would have a pH of 4,76. It wouldn't matter what the concentrations were, as long as ethanoate in solution. they were the same. It can change the pH of the buffer solution by changing the ratio of acid to salt, or by choosing a different acid and one of its salts. Ethanoic acid is a weak acid, and the position of this equilibrium will be to the left:

$$CH_3COOH_{(aq)} \leftrightarrow H_{(aq)} + \; CH_3COO_{(aq)}$$

Email: Zahraa.Salah.Hadi@uomus.edu.iq

a-Adding sodium ethanoate to this adds lots of extra ethanoate ions.

According to Le Chatelier's Principle, that will tip the position of the equilibrium even future to the left. the solution will Therefore contain these Important things:

- Lots of un-ionized ethanoic acid.
- Lots of ethanoate ions from sodium ethanoate.
- Enough hydrogen ions to make the solution acidic.

b-Adding an acid to this buffer solution

The buffer solution must remove most of the new hydrogen ions otherwise the pH would drop markedly. Hydrogen ions combine with the ethanoate ions to make ethanoic acid. Although the reaction is reversible, since ethanoic

Email: Zahraa.Salah.Hadi@uomus.edu.iq

acid is a weak acid, most of the new hydrogen ions are removed in this way so the pH won't change very much but because of the equilibrium involved, it will fall a little bit.

$$CH_3COO^-_{(aq)} + H^+ \leftrightarrow CH_3COOH_{(aq)}$$

c-Adding an alkali to this buffer solution

Alkaline solutions contain hydroxide ions and the buffer solution removes most of these. This time the situation is a bit more complicated because there are two processes which can remove hydroxide ions.

- **Removal by reacting with ethanoic acid**

  The most likely acidic substance which a hydroxide ion is going to collide with is an ethanoic acid molecule. They will react to form ethanoate ions and water.

$$CH_3COOH_{(aq)} + OH^-_{(aq)} + H_2O_{(l)}$$

Because most of the new hydroxide ions are removed, the pH doesn't increase very much.

Remember that there are some hydrogen ions present from the ionization of the ethanoic acid.

- **Removal of the hydroxide ions by reacting with hydrogen ions**

  Hydroxide ions can combine with these to make water. As soon as this happens, the equilibrium tips to replace them. This keeps on happening until most of the hydroxide ions are removed

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Example 1:

You are given a buffer solution containing 0.2 M acetic acid (CH_3COOH) and 0.2 M sodium acetate (CH_3COONa). The pKa of acetic acid is 4.76.

Calculate the pH of the buffer solution.

Solution 1:

We can use the **Henderson-Hasselbalch equation**:

$$\mathrm{pH} = \mathrm{pKa} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

Where:

- **pKa = 4.76** (for acetic acid)
- $[\mathrm{A}^-]$ (sodium acetate) = 0.2 M
- $[\mathrm{HA}]$ (acetic acid) = 0.2 M

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- $[\mathrm{HA}]$ (acetic acid) = 0.2 M

Substitute values into the equation:

$$\mathrm{pH} = 4.76 + \log\left(\frac{0.2}{0.2}\right)$$

$$\mathrm{pH} = 4.76 + \log(1) = 4.76 + 0$$

$$\mathrm{pH} = 4.76$$

So, the **pH** of the buffer solution is **4.76**.

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Example 2 :

You have a buffer solution made by mixing 0.1 M ammonia (NH_3) and 0.1 M ammonium chloride (NH_4Cl). The pKa of ammonia is 9.25.

Calculate the pH of this buffer solution.

Solution 2:

Using the **Henderson-Hasselbalch equation**:

$$\mathrm{pH} = \mathrm{pKa} + \log\left(\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}\right)$$

Where:

- **pKa = 9.25** (for ammonia)
- $[\mathrm{A}^-]$ (ammonia, NH_3) = 0.1 M
- $[\mathrm{HA}]$ (ammonium chloride, NH_4Cl) = 0.1 M

Substitute values into the equation:

$$\mathrm{pH} = 9.25 + \log\left(\frac{0.1}{0.1}\right)$$

$$\mathrm{pH} = 9.25 + \log(1) = 9.25 + 0$$

$$\mathrm{pH} = 9.25$$

So, the **pH** of the buffer solution is **9.25**.

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Example 3:

You add 0.01 mol of HCl to 1 liter of a buffer solution containing 0.2 M ammonia (NH_3) and 0.2 M ammonium chloride (NH_4Cl). The pKa of ammonia is 9.25.

Calculate the new pH of the buffer after the addition of HCl.

Solution 3:

1. **Before adding HCl:** The pH before the addition of HCl can be calculated using the Henderson-Hasselbalch equation:

$$\mathrm{pH} = 9.25 + \log\left(\frac{0.2}{0.2}\right) = 9.25$$

2. **After adding HCl:** HCl, being a strong acid, will donate H^+ ions, which will react with ammonia (NH_3, the base) to form ammonium ions (NH_4^+). The amount of NH_3 will decrease, and the amount of NH_4^+ will increase.

- Initially: $[\mathrm{NH_3}] = 0.2\,\mathrm{mol/L}$ $[\mathrm{NH_4Cl}] = 0.2\,\mathrm{mol/L}$
- When 0.01 mol of HCl is added to the buffer, it will react with 0.01 mol of NH_3 to form NH_4^+.

$$[\mathrm{NH_3}] = 0.2 - 0.01 = 0.19\,\mathrm{mol/L}$$

- The amount of NH_4^+ will increase by 0.01 mol:

$$[\mathrm{NH_4Cl}] = 0.2 + 0.01 = 0.21\,\mathrm{mol/L}$$

3. **New pH calculation:**

Now, we can use the Henderson-Hasselbalch equation again:

$$\mathrm{pH} = 9.25 + \log\left(\frac{0.19}{0.21}\right)$$

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First, calculate the ratio:

$$\frac{0.19}{0.21} = 0.9048$$

Now, find the logarithm:

$$\log(0.9048) = -0.0433$$

Substitute into the equation:

$$\mathrm{pH} = 9.25 + (-0.0433) = 9.2067$$

So, the new **pH** of the buffer solution after adding HCl is approximately **9.21**.

Example 4:

You have a buffer solution of 0.4 M acetic acid (CH_3COOH) and 0.4 M sodium acetate (CH_3COONa). You add 0.05 moles of NaOH to 1 liter of the buffer solution. The pKa of acetic acid is 4.76.

Calculate the pH of the buffer solution after the addition of NaOH.

Solution :

1. **Before adding NaOH:** The pH of the buffer solution can be calculated using the Henderson-Hasselbalch equation:

$$\mathrm{pH} = 4.76 + \log\left(\frac{0.4}{0.4}\right) = 4.76$$

2. **After adding NaOH:** NaOH will dissociate into OH^- ions, which will neutralize the acetic acid (CH_3COOH). The reaction is:

$$\mathrm{CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O}$$

- Amount of NaOH added = 0.05 mol (this is also the amount of OH^- added).
- This will react with an equivalent amount of acetic acid (CH_3COOH), so the new concentrations will be:
  - $[\mathrm{CH_3COOH}] = 0.4 - 0.05 = 0.35\,\mathrm{mol/L}$
  - $[\mathrm{CH_3COO^-}] = 0.4 + 0.05 = 0.45\,\mathrm{mol/L}$

3. **New pH calculation:** Using the Henderson-Hasselbalch equation again:

$$\mathrm{pH} = 4.76 + \log\left(\frac{0.45}{0.35}\right)$$

Calculate the ratio:

$$\frac{0.45}{0.35} = 1.2857$$

Now, find the logarithm:

$$\log(1.2857) = 0.1083$$

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Substitute into the equation:

$$pH = 4.76 + 0.1083 = 4.8683$$

So, the new pH of the buffer solution after adding NaOH is approximately **4.87**.

Email: Zahraa.Salah.Hadi@uomus.edu.iq