Experiment 21

BUFFER SOLUTIONS

***Key concepts**: Chemical equilibria, Thermodynamic equilibrium constant, Activity systems. Chemical potential. Mean electrolyte activity. Electrolytic dissociation. Strong and weak electrolytes. Brönsted and Lewis theories of acids and bases. Self-ionization of water.. pH scale and its measurement. Buffer solutions and their mechanism of action.*

Buffer solutions are solutions that retain a practically constant pH value, despite dilution or addition of certain amounts of strong acid or strong base. The simplest systems behaving in this way contain: a weak base and a salt of this base with a strong acid, or a weak acid and a salt of this acid with a strong base. We will discuss the latter case in further considerations.

Thermodynamic equilibrium constant for the dissociation of a weak acid in aqueous solutions:

$$HA + H_2O \leftrightarrow A^- + H_3O^+ \qquad (1)$$

according to the law of chemical equilibrium, can be described using the shortened equation:

$$K_a = \frac{a_{H_3O^+} \cdot a_{A^-}}{a_{HA}} \qquad (2)$$

where $a_{H_3O^+}$, a_{A^-} and a_{HA} are the equilibrium activities of the H_3O^+ and A^- ions and HA molecules (respectively), related to the standard concentration ($c^{\ominus} = 1$ mol dm^{-3}) and therefore dimensionless quantities.

After taking the logarithm of equation (2) and transforming, we get:

$$pH = pK_a + log\frac{a_{A^-}}{a_{AH}} \qquad (3)$$

where $pK_a = -logK_a$

If the buffer solution contains a weak acid and a salt of this acid with a strong base, the presence of anions (A^-) coming from the completely dissociated salt causes the reaction equilibrium (1) shifted to the left. The weak acid in the buffer solution therefore exists almost entirely in the form of undissociated molecules (*HA*).

At a not very high concentration of components (≤ 0.1 mol dm^{-3}) in the buffer mixture, their average activity coefficients are close to unity ($\gamma_{\pm} \approx 1$). For that reason, we can replace the activity of a weak acid with its concentration ($a_{HA} = c_k$), and replace the activity of anions with the salt concentration ($a_{A^-} = c_s$). As a consequence, from equation (3) we can get:

$$pH = pK_a + log\frac{c_s}{c_k} \qquad (4)$$

We note that the *pH* of a buffer solution depends only on the concentration ratio of salt and acid, not from their absolute value. Since the quotient (c_s/c_k) appears in the formula under the logarithm, even when the concentration ratio is changed a hundred times, from 1:10 to 10:1, the pH value changes only by 2 units.

Table 1. Dependence of the pH of the buffer solution on the ratio of salt and acid concentration

$c_s : c_k$	pH
1:10	$pK_a + log0,1 = pK_a - 1$
1:1	$pK_a + log1 = pK_a$
10:1	$pK_a + log10 = pK_a + 1$

Adding a certain amount of strong acid to the considered buffer solution causes an increase in the concentration of the weak acid in the solution (c_k) and a simultaneous decrease in the salt concentration (c_s) as a result of the reaction:

$$H_3O^+ + A^- \rightarrow H_2O + HA \tag{5}$$

In turn, the addition of a strong base has the opposite effect, because the following reaction occurs:

$$OH^- + HA = H_2O + A^- \tag{6}$$

In both cases, there is only a slight change in the pH of the buffer. However, it is not related to the introduction of either H_3O^+ or OH^- ions, which are neutralized, but to a change in the concentration ratio (c_s/c_k).

It is important that although the number of moles of a strong acid or strong base added to this type of buffer solution causes a change in both c_k and c_s, the total (combined) concentration of these components c_c remains constant:

$$c_c = c_k + c_s \tag{7}$$

After substituting $c_k = c_c - c_s$ into equation (4), with the simultaneous conversion of common logarithms to natural logarithms, we obtain:

$$pH = pK_a + 0,4343 ln \frac{c_s}{c_c - c_s} \tag{8}$$

The above equation shows the dependence of the pH of the buffer solution on the salt concentration (c_s), for a given total concentration of buffer components (c_c). After differentiating with respect to the salt concentration and presenting the result as the inverse, we obtain [1] :

$$\frac{dc_s}{d(pH)} = \frac{1}{0,4343} \cdot \frac{c_s(c_c - c_s)}{c_c} \tag{9}$$

The expression on the left side of the equation is referred to as **buffer capacity** (β), which is a measure of the buffer's resistance to pH changes due to the addition of a strong acid or strong base. We define buffer capacity as the number of moles of hydrogen or hydroxide ions, added to 1 dm^3 of buffer, required to change the pH of the solution by one unit. Since the addition of H_3O^+ ions causes a decrease in the concentration of anions coming from weak acid salts, and the addition of OH^- ions causes their corresponding increase, in practice the buffer capacity is often expressed as the ratio of the finite change in salt concentration (Δc_s) to the corresponding change (*ΔpH*) buffer solution when adding a strong acid or strong base [2]:

$$\beta = \frac{dc_s}{d(pH)} \cong \frac{\Delta c_s}{\Delta(pH)} \tag{10}$$

The combination of equation (9) and (10) results in:

$$\beta = \frac{1}{0{,}4343} \cdot c_s \frac{c_c - c_s}{c_c} = 2{,}303 \cdot c_s \left\{1 - \frac{c_s}{c_c}\right\} \tag{11}$$

To find the maximum of the function β = *f* (c_s), we differentiate equation (11), and obtain:

$$\frac{d\beta}{dc_s} = 2{,}303 \left\{1 - \frac{2c_s}{c_c}\right\} \tag{12}$$

It can be noticed that $\frac{d\beta}{dc_s} = 0$, when $1 - \frac{2c_s}{c_c} = 0$. Therefore, for $c_s = \frac{c_c}{2}$ and taking into account equation (7), the maximum buffer capacity is a buffer solution containing acid and salt of equal concentrations ($c_s = c_k$). We can thus calculate the value of the maximum buffer capacity (β_{max}) by substituting ($c_s = 0{,}5 \cdot c_c$) into equation (11):

$$\beta_{max} = 2{,}303 \cdot 0{,}5 \cdot c_c \left\{1 - \frac{0{,}5 \cdot c_c}{c_c}\right\} = 0{,}576 \cdot c_c \tag{13}$$

After substituting ($c_s = 0{,}5 \cdot c_c$) into equation (8), we obtain the pH value of the solution with the maximum buffer capacity:

$$pH_{\beta_{max}} = pK_a \tag{14}$$

The buffering capacity of the mixture increases with the increase in the total concentration of buffer components (c_c). The more concentrated the solution, the smaller the relative changes in the concentration of the weak acid and salt due to the addition of equal amounts of a strong acid or strong base. Therefore, dilution of the buffer, although it does not cause a change in pH, reduces its buffer capacity. The buffer is effective when its pH is in the range ($pH = pK_a \pm 1$), i.e. when the salt to acid concentration ratio is from 0,1 to 10. In order to prepare a buffer solution with a given *pH*, select a system for which pK_a is close to the desired *pH* value and, based on equation (4), calculate the ratio of salt and acid concentration in the solution. In practice, solutions with a maximum total concentration (c_c) of the order of 0,1 – 0,2 mol dm^{-3} are used, for which the activity coefficients are not much different from the value of 1.

Experimental section

The aim of the exercise is to study the dependence of the capacity of an acetate buffer ($CH_3COOH + CH_3COONa$) on its composition, based on *pH* measurements before and after adding the same amount of strong acid to a series of buffer solutions with a constant total concentration of buffering components, but a different ratio of salt and acid.

Calibration of the pH-meter

Before starting the experiment, we calibrate the pH-meter. Calibration is performed using standard buffer solutions of known *pH*.

After connecting the pH-meter to the power and turning on the instrument's power supply, you should:

1. depending on the type of pH-meter, press the "pH" button or set the range switch to the "pH 0...14" position,
2. connect a combined glass electrode (combined with the reference electrode) to the pH-meter,
3. wash the electrode with distilled water several times, changing the distilled water in a clean beaker about 5 times and each time moving the electrodes vertically and horizontally (we do this after each change of the standard or test solution). After drying with tissue paper, place the electrodes in a vessel containing a standard solution with pH ≈ 7, moving them several times (vertically and horizontally) in this solution to provide equal concentration in the whole volume. Then calibrate the pH-meter according to the calibration instructions located next to the pH-meter
4. after rinsing and transferring the electrode to a standard solution with pH = 4 (if measurements are to be carried out in an acidic environment) or pH = 10 (before measurements in an environment with pH > 7), use the same procedure as in point 3 to set the pH value of this solution,
5. repeat the steps described in points 3 and 4, checking the correctness of the instrument's readings,
6. after completing steps 1-5, you can proceed to pH measurements of the investigated solutions.

Methodology

Prepare thirteen investigated buffer solutions of 25 cm ^{3} each one (see Table 2), using the provided solutions of CH_3COOH with a concentration of c_k^p = 0,02 mol dm^{-3} and CH_3COONa with a concentration of c_s^p = 0,02 mol dm^{-3}.

Fill the 13 beakers with the particular volumes of acetic acid solution (V_k) and sodium acetate solution (V_s), which are given in Table 2, directly from the burettes. The calculated values of the CH_3COOH concentration in a proper buffer solution: ($c_k = c_k^p \cdot V_k/(V_k + V_s)$) and the corresponding CH_3COONa concentration: ($c_s = c_s^p \cdot V_s/(V_k + V_s)$) should be listed in Table 2.

Place a magnetic stirrer and a combine electrode (after rinsing it with distilled water, see point 3 above) into a beaker containing 25 cm^3 of the first investigated buffer solution. When the pH value becomes stable, it should be read as pH_0 and listed in Table 2.

Then, using an automatic pipette, add (V_{HCl}) 0,5 cm^3 of a HCl solution (c_{HCl} = 0,1 mol dm^{-3}) into the investigated buffer solutions. The reaction described by equation (5) occurs. After mixing the solution (magnetic stirrer), wait about 30 - 60 seconds to obtain stationary conditions and read the pH_i value.

Place the calculated absolute value of the change (decrease) in the concentration of CH_3COO^- (Δc_s) ions formed from the dissociation of the CH_3COONa salt, occurring as a result of addition of HCl to the volume ($V_c = V_k + V_s$) of the buffer solution: ($\Delta c_s = (V_{HCl} \cdot c_{HCl})/(V_c + V_{HCl})$) in Table 2.

Proceed for all subsequent studied buffer solutions in the same way.

Table 2. Measurements

No	V_s [cm ^{3}]	V_k [cm ^{3}]	c_s $\left[\frac{mol}{dm^3}\right]$	c_k $\left[\frac{mol}{dm^3}\right]$	c_s/c_k	pH_0	pH_i	$\Delta pH = \lvert pH_i - pH_0 \rvert$	$\lvert \Delta c_s \rvert$	β
1	3,5	21,5								
2	5,0	20,0								
3	6,5	18,5								
4	8,5	16,5								
5	10,5	14,5								
6	12,5	12,5								
7	14,5	10,5								
8	16,5	8,5								
9	18,5	6,5								
10	20,0	5,0								
11	21,5	3,5								
12	23,0	2,0								
13	23,5	1,5								

The correctness of the measurements can be checked by comparing the pH values measured for the two extreme buffer solutions (before adding hydrochloric acid) with the values calculated based on equation (4). It is known that for CH_3COOH at temperature T = 298 K, K_a = 1.810^{-5}, with $a^{\ominus}$ = 1 mol dm^{-3} .

<u>Calculations</u>

Based on the experimental data from Table 2, we calculate the buffer capacity of the subsequent tested buffer solutions using formula (10) and prepare a graph of the dependence of β as a function of pH. The value of $\beta_{\max}$ taken from the graph should be compared with the value calculated according to equation (13). Moreover, taking into account equation (14), the pH value corresponding to $\beta_{\max}$ (read from the same graph) should be compared with the theoretical value of pK_a.

Supplement

1) $\frac{c_s}{c_c - c_s} = u$

$pH = pK_a + 0{,}4343 \cdot lnu$ and $\frac{d(pH)}{dc_s} = \frac{d(pH)}{du} \cdot \frac{du}{dc_s}$

by substituting the derivatives:

$\frac{d(pH)}{dc_s} = \frac{0{,}4343}{u}$ and $\frac{du}{dc_s} = \frac{c_c}{(c_c - c_s)^2}$

into the last equation, we obtain equation (10).

2) $\frac{d\beta}{dc_s} = 2{,}303\left[1 - \frac{c_s}{c_c}\right] + 2{,}303c_s\left[-\frac{1}{c_c}\right] = 2{,}303\left[1 - \frac{2c_s}{c_c}\right]$