pH buffers. Buffer capacity and buffering range

1. Introduction

Buffer solutions are aqueous solutions, consisting of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid. An important property of buffer solutions is its ability to maintain a relatively constant pH value in response to the addition of small amount of acid or base. Additionally, the pH of the buffer solutions remains relatively stable also during dilution. For this reason, buffer solutions are used in a wide range of chemical applications, primarily as reagents that allow to maintain a constant pH value (in the production of dyes, in fermentation processes, as well as to set the pH of food products, cosmetics and medicines).

The pH of the buffer depends on the pK_a of the acid (or pK_b of the base) as well as the ratio of acid (base) and its conjugate base (acid) concentrations. This dependence is described by the Henderson-Hasselbalch equation. Considering the following reaction (in this example the buffer solution is prepared using weak acid) :

$$\mathrm{HA} + \mathrm{H_2O} \leftrightarrow \mathrm{H_3O^+} + \mathrm{A^-}$$

the Henderson-Hasselbalch’s equation looks as follows:

$$\mathrm{pH} = \mathrm{pK_a} + \log_{10}\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

where:

$[A^-]$ – concentration of conjugate base [mol·dm^{-3}],

[HA] – concentration of acid (undissociated) [mol·dm^{-3}],

pK_a – negative logarithm of K_a value (K_a – acid dissociation constant).

Example for acetic acid:

$$\mathrm{CH_3COOH} + \mathrm{H_2O} \leftrightarrow \mathrm{H_3O^+} + \mathrm{CH_3COO^-}$$

$$\mathrm{pH} = \mathrm{pK_a} + \log_{10}\frac{[\mathrm{CH_3COO^-}]}{[\mathrm{CH_3COOH}]}$$

The pK_a value is a quantitative information of the acid strength. It is assumed that weak acids have pK_a values greater than 3 (-log(0.001) = 3). The higher the pK_a value, the weaker the acid. Based on the Henderson-Hasselbalch equation, it can be seen that the pH of the buffer solution is equal to the pK_a value of the acid, when the ratio of undissociated acid concentration to the anion concentration (resulting from the dissociation of this acid) equals 1, because log(1) = 0.

In the case of weak acid titration with a strong base, this situation occurs after adding the amount of base equal to half of the amount needed to completely neutralize the acid, i.e.

when the titration rate is 50% (Fig. 1). In addition, the pH of the solution changes relatively slowly in the buffering range, *ie* at pH = $pK_a \pm 1$.

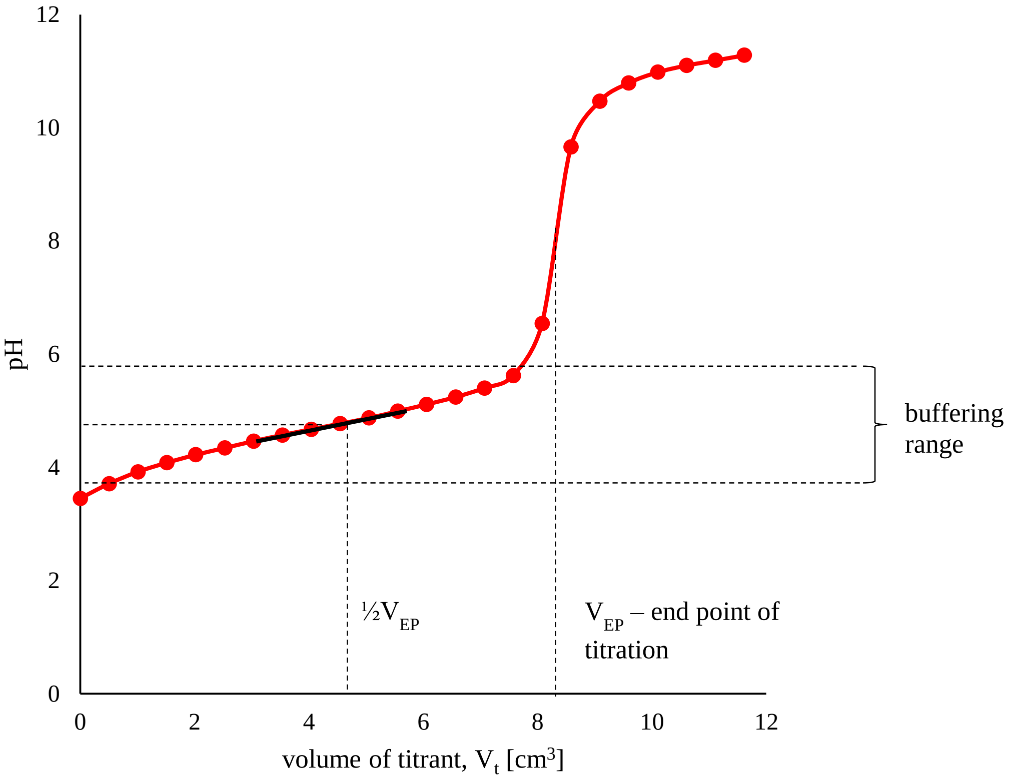

Fig. 1. Example of weak acid titration curve. Titration of acetic acid solution (pK_a = 4.7) with strong base (*e.g.* NaOH).

However, addition of too big amount of an acid or base to a buffer solution will lead to an overload of a buffer causing a significant change in the pH of the solution.

The term "buffer capacity" (β) quantifies the change in pH of the solution caused by the addition of a strong acid or base. It is calculated in relation to 1 dm^3 of a buffer solution.

$$\beta \approx \left|\frac{\Delta n}{\Delta pH}\right|$$

β – buffer capacity,

Δn – amount of added acid/base to the buffer solution [mol],

ΔpH – pH change cause by the addition of acid/base.

The value of the buffer capacity is strongly related to the concentrations of ingredients used and increases with their increase. Buffer solutions with a pH equal to the pK_a value of the acid (used to make this solution) have the greatest buffering capacity.

During the classes, students will perform pH-meter calibration, titration of weak organic acid samples, determination their pK_a values and buffer capacity.

2. Instructions

a) pH-meter calibration

Labware:

- pH-meter (1 piece)
- combined glass electrode (1 piece)
- magnetic stirrer with a stirring bar (1 piece)
- beaker 250 cm^3 (1 piece)
- wash bottle with distilled water (1 piece)
- paper towel (to be brought by the students)

Reagents:

- buffer solution, pH = 4.01
- buffer solution, pH = 7.00

Mount the combined glass electrode in the holder. Thoroughly rinse the electrode with distilled water and gently dry with a piece of paper towel. Place the vial with buffer solution (pH 4.01) on the magnetic stirrer. Immerse the glass electrode in the buffer solution (the electrolytic key must be submerged). Turn on the mix (moderate speed). Switch on the pH-meter and set it to the pH measurement mode (press the pH key). Wait until the pH meter readings stabilize. Go to the pH-meter calibration mode by holding down the pH key until the display shows "CAL" flashing. Press the "Enter" key. The display will show "P1" for a brief moment, defining the first calibration point. After a moment, the word "P1" will be replaced with a numerical value. This value corresponds to the pH of the first calibration solution. Use the (+) and (-) keys to set the pH of the first buffer solution (4.01). Press the Next key. The display will start showing the EMF of the measuring cell. Wait until it stabilizes. Confirm the obtained value by pressing the "Enter" key. After pressing this key, the pH meter will start EMF measurement for the second buffer solution. "P2" will appear briefly on the display. After a while, the inscription "P2" will be replaced with a numerical value. This value is the pH corresponding to the second calibration solution. Use the (+) and (-) keys to set the pH of the second buffer solution (7.00).

Before measuring for the second buffer solution, remove the electrode from the first buffer solution, thoroughly rinse it with distilled water and gently dry with a piece of paper towel. After these steps, the electrode can be placed in a vial with a second buffer solution.

Press the "Next" key. The display will start showing the EMF of the measuring cell. Wait until this value stabilizes and then confirm it by pressing the "Enter" key. After pressing this key, the pH-meter repeats the calibration procedure (EMF measurement for the first buffer solution). To stop, press the "pH" key. After the calibration of the pH-meter, remove the electrode from the buffer solution and rinse it thoroughly with distilled water.

b) titration of a weak acid

Labware:

- pH-meter (1 piece)
- combined glass electrode (1 piece)
- magnetic stirrer with a stirring bar (1 piece)
- beaker 250 cm^3 (1 piece)
- beaker 50 cm^3 (1 piece)
- wash bottle with distilled water (1 piece)
- paper towel (1 piece)
- 50 ml polyethylene containers (2 pieces)
- pipette 0.5 cm^3 (1 piece)

Reagents:

- NaOH solution (0.1 $mol \cdot dm^{-3}$)
- monocarboxylic, weak organic acid

Add approximately 100 mg and 500 mg of acid to separate polyethylene containers. Record the exact weight of the acid. To each container, gently add enough distilled water to completely dissolve the acid. The final volume of the solution should be 100 cm^3. Take care when dissolving the acid (do not spray it in the air, e.g. by too rapid adding water from the wash bottle).

Place the first container with the acid on the magnetic stirrer. Gently place inside the stirring bar. Then immerse the combined glass electrode (the electrolytic key must be submerged). Start stirring, wait until the pH-meter readings stabilize, then write down the pH value. Start the titration of the sample adding portions of 0.5 cm^3 of NaOH solution. After adding each portion of titrant, wait until the pH-meter readings stabilize. Write down the displayed pH value. The titration should be continued until a rapid increase of pH value is observed. After confirming this fact, add 4 more portions of the titrant. Repeat the titration for the other sample.

Attention! After completing each titration, rinse the electrode and the magnetic stirrer thoroughly.

Report must contain:

- introduction (examples of the use of buffer solutions in analytical chemistry),

- description of experiment,

- results (calculations, titration curves, reference of obtained results to literature values),

- conclusions.

Students are obliged to prepare report within one week after laboratories.