

Investigation of buffer capacity

Literature: ?????

Type of the practice: Individual.

Aim of the practice: Understanding the concept of buffer capacity and the precise determination of the buffer capacity of a buffer solution (or one of its component) found in the Hungarian Pharmacopoeia either experimentally or by calculation.

1 Introduction

Both the English and the Hungarian literatures use two definitions for determining the buffers.¹ According to the first definition, the buffers are such solutions, the pH of which remains almost constant if a small amount of either acid or base is added into it. The second definition uses the Brønsted-Lowry acid-base concept: the buffer is a solution containing a conjugated pair which can be either a weak acid and its conjugated base or a weak base and its conjugated acid. Fortunately, the different literatures are in good agreement about the essence of the buffer capacity: it is a number to characterize the ability of the buffer to stand up against the pH change of different processes. The buffer capacity must be a quantitative property, however, there are more definitions in the recent literature which are in contradiction to each other.

Corresponding to the most frequent definition, the buffer capacity is the amount of strong acid or strong base which can be added into a buffer solution without significant change in pH . This definition, however, leaves the meaning of the 'significant change' expression unanswered, and there is not a generally appropriate answer for this question. In some cases, even 2-3 pH -units change can be omitted, in other cases, 0.1-unit change can be significant. For example, the pH of the commercial soap solutions varies in the range of 5.4-8.5 (!). In contrast, the pH of the human blood must be in the range of 7.35-7.45. As small as 0.2 pH -unit deviation can cause serious illness, moreover 0.3 pH -unit deviation may lead to death. Biological buffers regulate the ideal pH -ranges in the living organisms.

Another frequent, more specific definition is that the buffer capacity is the amount of strong acid or strong base to be added to 1 dm³ solution to change its pH by one unit. Although this definition is frequently used in practice, it is clearly ambiguous because of the following three reasons:

1. The definition does not give the direction of the change in pH when acid or base is added.
2. The definition - except for rare cases - gives different numerical values as buffer capacity depending on if acid or base is added. The phrasing of the definition, however, suggests the parity of the acid and the base.
3. The most important deficiency of the second definition is that several slightly different phrasings of it exist, but these small deviations lead to different numerical values or even different units!²

The source of the above contradictions is that the original and precise phrasing of the definition of the buffer capacity is simplified in several ways (mainly in analytical textbooks), but during the simplification significant portions are omitted. To avoid the contradictions, the original defining equation of the puffer capacity (B_C)³ is used throughout this experiment. This equation can be given in the following form:

¹This summary is based on eight Hungarian textbooks and two English ones, as well as five English description presented on the Internet.

²The analysis of these different phrasings is not indented here so only two examples are given for the sake of clarity: (1) The buffer capacity is the amount of strong acid/base (expressed in mol/dm³) necessary to produce one unit change in pH . (2) The buffer capacity is the necessary volume of 1M strong acid or 1 M strong base (expressed in cm³) to change the values of pH of a buffer solution by one.

³The literature usually denotes the buffer capacity as β . It can easily be mixed with the stability product of the protonation; therefore BC is used to denote the buffer capacity throughout this document.

$$B_C = \frac{dn}{dpH} \left(= \frac{d(c_b \cdot (1dm^3))}{dpH} = \frac{-d(c_s \cdot (1dm^3))}{dpH} \right) \quad (1)$$

where n is the amount of monoprotic strong base (given in mol) added to $1dm^3$ buffer solution. Since the addition of strong acid is equivalent to the subtraction of strong base, therefore the amount of strong acid added corresponds to $-n$. The numerical value of this amount of substance equal to the molar concentration of the strong base added (c_b) or to the negative molar concentration of the strong acid added ($-c_s$) as shown by equation (1). This consideration and phrasing the definition in differential form prove that (1) the numerical value is the same in case of adding either acid or base, as well as (2) the value of the buffer capacity is always positive with the unit of the amount of substance. In the followings, concentrations are used in all formulas, but for the sake of simplicity, the volume is not always indicated for the sake of simplicity. *but it is always implied!*

2 Determination of buffer capacity by calculation

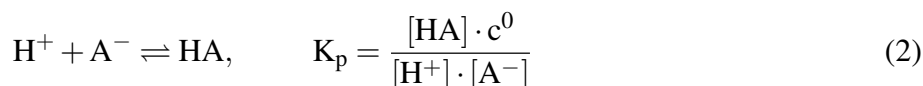
This section gives the formulas necessary to calculate the buffer capacity. The deductions require the knowledge of the following notions and definitions (most of them are already known from analytical chemistry):

- The *total concentration* (T) of a substance means the overall concentration of that substance independently from its forms. For example, if a solution contains the AB, AB₂ and AB₃ substances composed from the A and B particles then the total concentration of B can be given by:

$$T_B = [B] + [AB] + 2 \cdot [AB_2] + 3 \cdot [AB_3]$$

equation using the equilibrium concentrations. The analytical methods, like weighting or volumetry, usually provide the total concentration as experimental data.

- The *protonation constant* (K_p) is the equilibrium constant of a protonation process.⁴ The process and its equilibrium constant for the anion of a monoprotic acid can be given by following equation:



where c^0 is the standard concentration.⁵

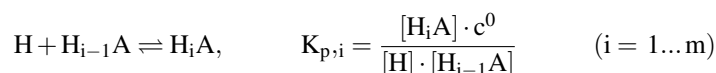
At first, B_C is formulated for the simplest case when the anion of a monoprotic acid is partially protonated in a solution with the volume of $1 dm^3$, and the amount of the strong base added into the solution is n . Before adding the base, the total concentrations of the hydrogen ion (T_H) and the anion of the acid (T_A) can be given by the

$$T_H = [HA] + [H^+] - [OH^-] = K_p \cdot [H^+] \cdot [A^-] + [H^+] - \frac{K_v}{[H^+]} \quad (3)$$

$$T_A = [HA] + [A^-] = K_p \cdot [H^+] \cdot [A^-] + [A^-] \quad (4)$$

⁴The equilibrium constant of the dissociation process is more frequently used in the analytical chemistry but the formulas to be deduced are simpler by using the protonation constants.

⁵In cases of polyprotic acids (where m is the number of the potential protons to be donated), the protonic equilibrium of their anion can be described by m processes and m equilibrium constants:



The charge numbers are not indicated for the sake of clarity.

equations if $[HA]$ and $[OH^-]$ are expressed and substituted from equation (2) and from the definition of the ionic product of water ($K_v = [H^+] \cdot [OH^-]$), respectively. The validity of equation (4) is obvious from the definition of the total concentration; however, equation (3) requires some explanation. There are two sources of the free H^+ : (1) the partial dissociation of the weak acid and (2) the self-ionization of water. The latter one is not included in the total concentration of the hydrogen ion since it is not added into the solution. The self-ionization of water produces the same amount of H^+ and OH^- therefore the $([H^+] - [OH^-])$ difference gives the concentration of hydrogen ion derived from the dissociation of the weak acid.

If $[A^-]$ is expressed from Eq.(4) $\left([A^-] = \frac{T_A}{1 + K_p \cdot [H^+]}\right)$, and it is substituted into equation (3) then

$$-T_H = \frac{K_v}{[H^+]} - [H^+] - T_A \cdot \frac{K_p \cdot [H^+]}{1 + K_p \cdot [H^+]} \quad (5)$$

the equation is reached after some rearrangements from which the $[H^+]$ (and also the pH) can be calculated knowing the total concentrations and the protonation constant.

If n amount of base is added into 1dm^3 buffer solution, then the value of T_H is decreased by this number since adding base into a solution is equivalent to taking acid from it:

$$\Delta n = \Delta(-T_H), \quad \text{illette} \quad dn = d(-T_H).$$

Based on some simplifications and mergers the calculation the buffer capacity can be given with the following equation:⁶

$$B_C = \ln(10) \cdot \left(\frac{K_v}{[H^+]} + [H^+] + \frac{T_A \cdot K_p \cdot [H^+]}{(1 + K_p \cdot [H^+])^2} \right).$$

According to this equation, the value of the buffer capacity is the function of the hydrogen concentration at a given buffer concentration. Since $[H^+]$ is changing in a range of more than ten orders of magnitude, the buffer capacity is more frequently expressed as the function of pH :

$$B_C = B_C(pH) = \ln(10) \cdot \left(\frac{K_v}{10^{-pH}} + 10^{-pH} + \frac{T_A \cdot K_p \cdot 10^{-pH}}{(1 + K_p \cdot 10^{-pH})^2} \right), \quad (9)$$

i.e., B_C is plotted as the function of pH so the buffer capacity is given by a diagram. In the followings, B_C is always regarded as a function of pH , but it is not indicated for the sake of simplicity.

It can be seen by analyzing equation (9) that the buffer capacity is the product of a constant and the sum of three terms. The numerical value of any quantity in these three terms can only be a non-negative number

⁶Eq.(1) can be changed with the help of $\Delta n = \Delta(-T_H)$, and $dn = d(-T_H)$ consideration, together with the differentiation rules of complex functions $\left(\frac{d f(g(x))}{dx} = \frac{d f(g)}{dg} \cdot \frac{dg(x)}{dx}\right)$:

$$B_C = \frac{dn}{dpH} = \frac{dn}{d[H^+]} \cdot \frac{d[H^+]}{dpH} = \frac{d(-T_H)}{d[H^+]} \cdot \frac{d[H^+]}{dpH}. \quad (6)$$

According to Eq.(5) and the quotient rule $\left(\frac{d\left(\frac{f(x)}{g(x)}\right)}{dx} = \frac{\frac{df(x)}{dx} \cdot g(x) - f(x) \cdot \frac{dg(x)}{dx}}{g^2(x)}\right)$:

$$\frac{d(-T_H)}{d[H^+]} = -\frac{K_v}{[H^+]^2} - 1 - \frac{T_A \cdot K_p}{(1 + K_p \cdot [H^+])^2}, \quad (7)$$

while using the definition of pH :

$$\frac{[H^+]}{c^0} = 10^{-pH} = e^{-pH \cdot \ln(10)}, \quad \frac{d[H^+]}{dpH} = -\ln(10) \cdot c^0 \cdot e^{-pH \cdot \ln(10)} = -\ln(10) \cdot [H^+]. \quad (8)$$

If we substitute the derivatives of Eq. (7) and (8) to Eq.(6) we can get the definition of the buffer capacity.

providing positive sign for the buffer capacity. Inside the large parentheses, the first and the second terms have large numerical values in basic and acidic solutions, respectively. It expresses that the buffer capacity is intrinsically large in either strong base or strong acid solution, so the added acid or base does not change the pH of the solution significantly, independently from the quality of the buffer. The third term characterizes the buffer itself, and it has large numerical value in different pH ranges, depending on the values of T_A and K_p .

If the buffer consists of the various protonated forms of a biprotic anion (A^{2-}) then the expression of B_C changes ⁷:

$$B_C = \ln(10) \cdot \left(\frac{K_v}{10^{-pH}} + 10^{-pH} + T_A \cdot K_{p,1} \cdot 10^{-pH} \cdot \frac{(1 + 4 \cdot K_{p,2} \cdot 10^{-pH} + K_{p,1} \cdot K_{p,2} \cdot 10^{-2 \cdot pH})}{(1 + K_{p,1} \cdot 10^{-pH} + K_{p,1} \cdot K_{p,2} \cdot (10^{-2 \cdot pH})^2)} \right) \quad (10)$$

The comparison of this formula and equation (9) clearly shows that the calculation of the buffer capacity is possible with a much more complicated expression in case of biprotic anions. Although the more complicated multiprotic anions also have practical importance as buffers (e.g., citrate and phosphate ions), these ones are not studied during the practice because of the complexity of the expression of B_C .

If a buffer solution consists of more substances, then the third term of them must be summarized. For example, if a buffer solution includes two monoprotic anions (A_1^- és A_2^-) with the total concentrations of T_{A_1} and T_{A_2} and with the protonation constants of K_{p1} és K_{p2} then the buffer capacity can be given by the:

$$B_C = \ln(10) \cdot \left(\frac{K_v}{10^{-pH}} + 10^{-pH} + \sum_{j=1}^2 \frac{T_{A_j} \cdot K_{pj} \cdot 10^{-pH}}{(1 + K_{pj} \cdot 10^{-pH})^2} \right) \quad (11)$$

equation. The same formula can be used if both the anion and the cation of the buffer take part of protonation processes. In this case, the total concentration should be calculated from the stoichiometric composition of the buffer salt.

3 Experimental determination of buffer capacity

If the protonation constants are unknown in a buffer solution, or the calculation seems to be more difficult (e.g., in cases of multiprotic anions) then the buffer capacity can also be determined experimentally by pH metric titration. This method is based on the differential form of the definition of the buffer capacity given in equation (1).

Let V_0 is the initial volume of the titrand and let c_b is the concentration of the titrant which is a strong base solution. Let V_j and V_{j+1} are the consumptions in two subsequent titration points and let pH_j and pH_{j+1} are their corresponding measured pH . Accordingly, the change of the added amount of the base between these two titration points is $c_b (V_{j+1} - V_j)$. By definition given in equation (1), the change of the amount of the base (Δn) applies to 1 dm^3 buffer solution which can be approximated by the:

$$\Delta n \cong c_b (V_{j+1} - V_j) \cdot \frac{1 \text{ dm}^3}{V_0 + \frac{V_{j+1} + V_j}{2}} \quad (12)$$

formula in the above case, if the $(V_{j+1} - V_j) \ll (V_0 + V_j)$ inequality is valid and the volumes are given in dm^3 . From similar considerations:

⁷In this case instead of Eq.(3) and (4) we use these equations

$$\begin{aligned} T_H &= 2 \cdot [H_2A] + [HA^-] + [H^+] - [OH^-] = 2 \cdot K_{p,1} \cdot K_{p,2} \cdot [H^+]^2 \cdot [A^{2-}] + K_{p,1} \cdot [H^+] \cdot [A^{2-}] + [H^+] - \frac{K_v}{[H^+]} \\ T_A &= [H_2A] + [HA^-] + [A^{2-}] = K_{p,1} \cdot K_{p,2} \cdot [H^+]^2 \cdot [A^{2-}] + K_{p,1} \cdot [H^+] \cdot [A^{2-}] + [A^{2-}] \end{aligned}$$

to express $-T_H$ -t. We differentiate the received expression according to $[H^+]$, then express B_C with Eq.(6) and (8).

Table 1: **Datas for titrand preparation and calculations.**

substances	c_p (M)	$V_{0,1\text{ M HCl}}$ (cm ³)	$\lg K_{p,1}$	$\lg K_{p,2}$	consumption of alkali V(cm ³)
boric acid	0,035 – 0,050	5,00	9,1	-	0; 0,3; 0,6;...;2,7; 3; 4; 5;...;25;
sodium-acetate	0,035 – 0,050	55,00	4,6	-	
ammonium-chloride	0,035 – 0,050	5,00	9,3	-	
oxalic acid	0,020 – 0,025	5,00	4,0	1,3	0; 1; 2;...;15; 15,5; 16; 16,5;...;25;
malonic acid	0,020 – 0,025	5,00	5,3	2,6	
succinic acid	0,020 – 0,025	5,00	5,3	4,0	
ammonium-acetate	0,020 – 0,025	30,00	9,3 és 4,6	-	0; 0,5; 1,0;...; 25

$$\Delta pH = pH_{j+1} - pH_j. \quad (13)$$

The differences given in expressions (12) and (13) should be substituted into equation (1) to get the formula for calculating the buffer capacity between two successive titrations points:⁸

$$B_c^{\text{measured}} = \frac{dn}{dpH} \approx \frac{\Delta n}{\Delta pH} = \frac{c_b(V_{j+1} - V_j)}{pH_{j+1} - pH_j} \cdot \frac{1 \text{ dm}^3}{V_0 + \frac{V_{j+1} + V_j}{2}}. \quad (14)$$

The task during the practice is to determine the buffer capacity of a buffer solution given by the instructor. The determination must be carried out by both calculation and experiments, through a *pH* metric titrations.

4 Student's measurement

From Table 1., the instructor assigns (1) the substance to be used, (2) the concentration of the buffer solution to be titrated within the given ranges and (3) the initial volume of the titrant between 30 – 40 cm³. In case of no specific instruction, these data are boric acid, 0.05 M and 35 cm³, respectively. The next tasks are to be carried out:

1. If they are not ready then 0.1 M HCl solution and 0.1 M NaOH solution must be prepared (with the minimum volume of 100 cm³).
2. 100 cm³ buffer solution with the concentration of c_p should be prepared in a volumetric flask by weighting the necessary amount from the assigned material. The solution should also contain the necessary volume of 0.1 M HCl solution which is given in the third column of Table 1.
3. The burette should be cleaned and filled with the 0.1 M NaOH solution.
4. The *pH* meter should be calibrated before the titration by using two buffer solutions with known *pH* values. If more buffers are available then the *pH*~4 and *pH*~10 ones are to be used, or the buffers having the closest *pH* values. *Do not calibrate with cold solutions, please wait while their temperatures reach the nearly room temperature value.*
5. During the *pH* metric titration, the previously given volume of the buffer solution should be titrated with the 0.1 M base solution. The real consumptions must be close to the planned ones which are enumerated in the last column of Table 1. The precise consumption and the measured *pH* should be written into the report at the titration points. If the measured volume slightly deviates from the planned

⁸Since this number is essentially an approximation of a differential, the same value is valid for the whole range determined by the two points.

one, then the measured one should be written and should be used during the calculations. Two parallel titrations should be done. For sample to be titrated, please use suitable beaker; both the sensor part of the pH electrode and the ceramic diaphragm should also be immersed into the solution.

5 Evaluation of the measured data

The experimental conditions, as well as the measured and calculated data should be summarized in the following table:

compound: $c_p = \dots \text{ M}$, $V_0 = \dots \text{ cm}^3$ $t_{\text{lab}} \dots \text{ }^\circ\text{C}$					
$V \text{ (cm}^3\text{)}$	pH^{measured}	$\frac{pH_j + pH_{j+1}}{2}$	$B_c^{\text{measured}} \text{ (mol)}$	$T_A \text{ (M)}$	$B_c^{\text{calculated}} \text{ (mol)}$

1. The first two columns of the table contain the data of the measured titration curve. The third column is the average of two consecutive measured pH values. These averages will be the independent variables during the further calculations and on the graphs.
2. The fourth column is the buffer capacity calculated from the experimental data by equation (14).
3. The fifth column of the table is the total concentration of the anion of the buffer investigated along the titration points. In the j^{th} row of the table, this value can be calculated by the help of the T_A expression.

$$T_A = c_P \cdot \frac{V_0}{V_0 + \frac{V_j + V_{j+1}}{2}}$$

4. The calculated values of the buffer capacity should be given in the last column of the table. Depending on the substance investigated, the student must decide if formula (9), (10) or (11) should be used to calculate this column. The T_A values must be used from the fifth column. The ionic product of water is to be calculated by equation (found in the appendix) supposing that the values of the ionic strength can be approximated by the value of c_p . The independent variables for the calculations come from the third column.
5. After the above table is completed, a graph should be created, including both the experimental buffer capacity and the calculated one as the function of the third column of the table. Finally, the similarities and the occasional deviations between the two plotted curves must be interpreted and or explained. It concerns all the three ranges of the curve determined by the strong acid, the base and the weak acid.

Possible test questions

1. Give the two different definitions of the buffers!
2. What is the essence of the buffer capacity?
3. Give the two definitions of the buffer capacity formulated in non-differential form and list their contradictions!
4. Give the original definition of the buffer capacity which does not lead to contradiction!
5. Define the total concentration!
6. What are the formulas of the total concentrations in the solution of a monoprotic weak acid, expressed with the equilibrium concentrations, the ionic product of water and the protonation constants?

7. What is the expression of the buffer capacity in the solution of a monoprotic weak acid?
8. How the buffer capacity is to be calculated at a given pH from the measured data of a pH metric titration curve?
9. 100 cm^3 $0,1\text{ M NaH}_2\text{PO}_4$ solution is mixed with 150 cm^3 $0,2\text{ M H}_3\text{PO}_4$ solution. What are the total concentrations of Na^+ , H^+ and PO_4^{3-} in the mixed solution?
10. Calculate the values of the buffer capacity at $pH = 7$ and $pH = 9$ in 0.08 M ammonium chloride solution!
 $K_v = 1,2 \times 10^{-14}$ és $K_p = 2 \times 10^9$.
11. 50 cm^3 of 0.05 M weak acid solution is titrated with 0.1 M NaOH solution. The measured pH values are 7.345 and 7.497 at the consumptions of 6.0 and 6.1 cm^3 , respectively. What value of the buffer capacity can be calculated in the solution at $pH = 7,421$?
12. Based on the data given in question 11., what is the total concentration of the anion of the weak acid at the given point?

Remark: The change of the ionic strength is neglected during this experiment. Its effect on the shape of the $B_C(pH)$ curves are small so it would be unnecessary to keep the ionic strength at constant value in a more complicated experiment.